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PAULA MONONEN AND PETER LOZOVIK (eds.)

ACIDIFICATION OF INLAND WATERS

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NATIONAL BOARD OF WATERS AND THE ENVIRONMENT
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Joensuu, Finland, 3–7 June 1991

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Abstract
In June 1991 the third Finnish-Karelian Symposium on water problems was held in Joensuu, Finland. The title of the symposium was "Acidification of inland waters". Acidification research programmes including results were presented in a total of 11 papers.

Keywords
Acidification, precipitation, deposition, phytoplankton, zooplankton, macrobenthos, aquatic vegetation, trace metals, fish, lakes, Karelia, symposium

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Sakord (nyckelord)
Försurning, nederbörd, deposition, växtplankton, djurplankton, bottendjur, vattenflora, tungmetaller, fiskar, sjöar, Karelen, symposium

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FOREWORD

The first Soviet–Karelian – Finnish symposium on water problems was held in Petrozavodsk in 1989 as the beginning of the cooperation between the Karelian Research Center of the Academy of Science, USSR, and the National Board of Waters and the Environment, Finland. The second symposium was held in Petrozavodsk in May 1990. The title of this symposium was 'Primary production of inland waters'.

The third symposium, 'Acidification of inland waters' was held in Joensuu, Finland, in June 1991. The meeting included a three day seminar during which acidification research programmes in Finland and Karelia were presented in 11 papers. Scientific excursions were organized, too.

The editors wish to thank all the authors who have made the papers presented at the symposium available for publication. We also wish to thank Ms. Jaana Kalm–Koponen and Ms. Tyyne Muhonen for technical assistance of the drawings, Ms. Tuula Ikonen and Ms. Helena Naumanen for editing the manuscripts, Ms. Laurie Stewart for revising the English and Ms. Taina Saarinen for translating and editing the Russian references.

Since June 1991 the official name of the Karelian Research Center of Academy of Science, USSR, Water Problem Department has been changed. The new name, Karelian Research Center, Russian Academy of Sciences, Northern Water Problems Institute, has been used in the articles.

Peter Lozovik Paula Mononen

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THE EFFECT OF ACIDIC DEPOSITION ON WATERS

Kaarle Kenttämies
National Board of Waters and the Environment
P.O.Box 250
FIN–00101 Helsinki, Finland

1 WATER ACIDITY IN FINLAND

It has been established that the acidification of waters as a result of air pollution started in certain parts of Europe already in the 1920's and 1930's. Acidification and fish kill were attributed to air pollution for the first time in Norway in the 1950's, but in the early years it was merely a question of a research hypothesis. The first measurements of deposition were made in Finland in the 1950's. However, sulphur deposition in the background areas of Finland was, at that time, still less than half the level in the 1960's and 1970's. Water acidification came to light as local phenomena in the southern part of Norway and along the west coast of Sweden at the end of the 1960's and latter half of the 1970's.

The idea of atmospheric load derived water acidification first came up in Finland at the beginning of the 1970's (Kenttämies 1973). An investigation of the extent of water acidification in Europe and North America was carried out in Finland for the Economic Council of Europe (Merilehto et al. 1988). Acidic lakes and rivers really only occur in Fennoscandia and in the mountainous regions of Central Europe (Fig. 1). The number of acidic watercourses varies rather widely, even in susceptible areas, depending on the abundance of watercourses. While there are about 5 000 acidic lakes in both Sweden and Finland, there are only 50 in earlier West Germany, 15 in Czechoslovakia, 20 in Switzerland and 24 in Italy! However, the different countries come closer to each other when the frequencies are presented as relative proportions. Thus, for instance, about 5% of the lakes in both Sweden and West Germany are acidic.

The bedrock and soil in the area are the factors which determine whether acidic deposition can also pollute the watercourses. The relative sparseness of areas sensitive to acidification thus restricts the acidification of waterways in most parts of Central, Southern and Eastern Europe to merely curiosities. On the other hand, the watercourses in those parts of Fennoscandia with granitic bedrock and a thin layer of overburden left by the last ice age, can be acidified by a relatively low level of acidic deposition.

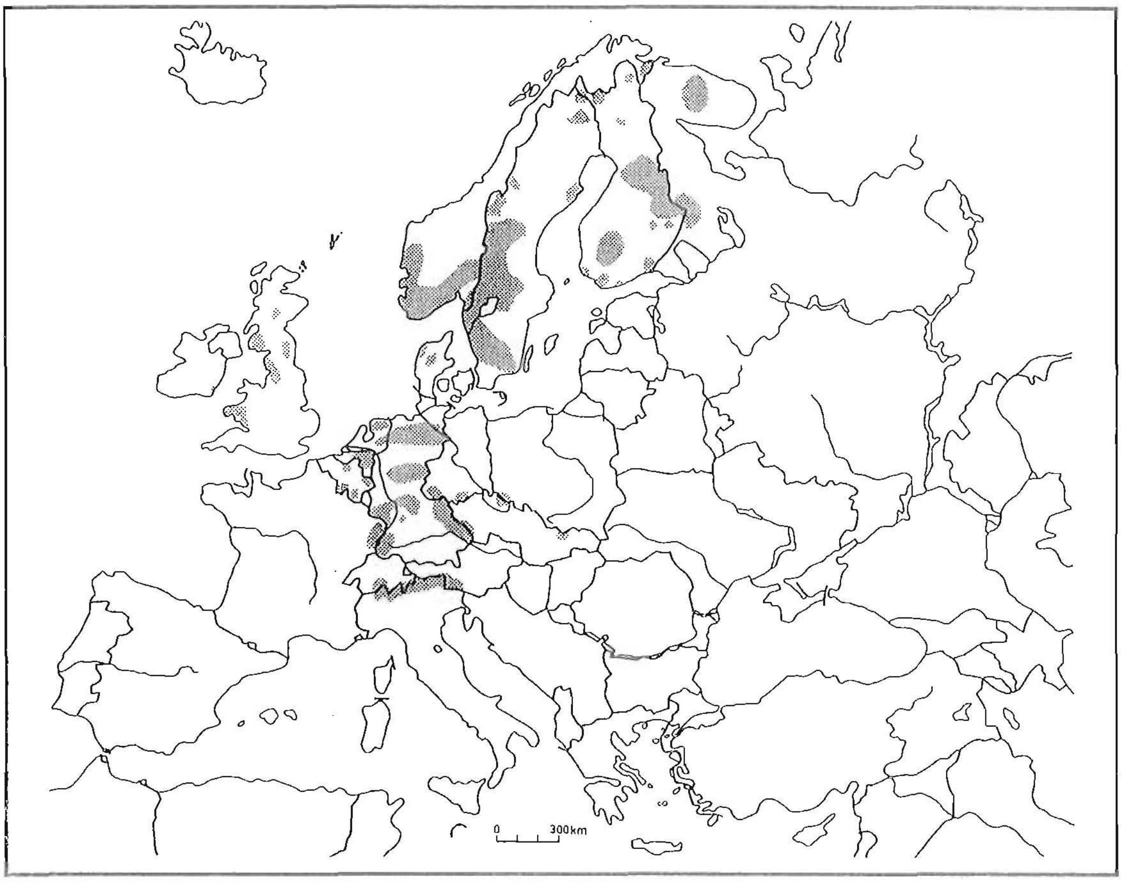

Fig. 1. Areas of Europe where acidic lakes and rivers are common. (Merilehto et. al. 1988).

2 NATURAL LEACHING AND ACIDIFICATION OF THE SOIL IN THE CATCHMENT AREAS OF SMALL FOREST LAKES

The state of the soil in about 200 small–lake catchment areas was investigated in the study. Extensive sampling was also used to obtain an overall picture of the buffering capacity of Finnish soil and bedrock. The catchment areas were surveyed, and the particle–size distribution, organic matter content, pH and exchangeable acidic and base cations of about 2 500 soil samples determined (Nuotio et al. 1990).

Carbonic acid and organic acids derived from the humus layer have been acidifying the surface soil, i.e. reducing its reserves of alkali and alkali–earth metals, already for thousands of years. The base saturation of the humus layer is, however, rather high because base cations (sodium, potassium, calcium and magnesium) are readily retained on the surface of the organic particles (Fig. 2). These base cations are primarily derived from decomposing plant remains and from deposition. The uplift of salts and water from the underlying mineral soil as a result of capillary forces is also possible on fine–textured soils, especially during the summer. The clay particles in fine–textured soils also have a high capacity to bind base cations, but these particles are almost completely lacking in coarse–textured soils. The base saturation of coarse–textured soils is derived from the small amount of intermixed clay material and the secondary minerals, dissolved out from the overlying soil layers, that have been reprecipitated on the surface of sand particles.

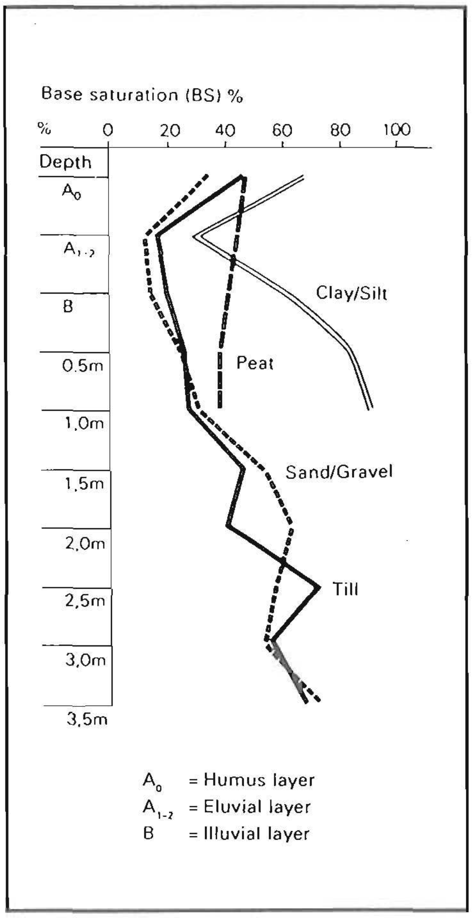

Fig. 2. Mean base saturation of podzolic soils in different zones and depths in Finland.

The illuvial layer, which lies immediately below the organic layer, has the lowest base saturation, but on moving deeper the situation improves to the extent that the base saturation already at a depth of 0.5 – 1.5 m corresponds to that of only slightly altered subsoil (Fig. 2).

Natural soil podzolisation is a slow process; 8 000 – 10 000 years after the last ice age the effects of this process are visible in the uppermost 10 cm-thick layer only. Owing to the variation in the level of the Baltic Sea, podzolisation has impoverished the soils in northern Finland for as much as 4000 years longer than those in southern Finland and along the coast of Ostrobothnia which were covered by the sea.

Anthropogenic soil acidification can, on the other hand, take place rapidly especially when the acid load is directed at types of soil that have already been subjected to natural acidification for a long period.

The effect of acidic deposition on the soil was most apparent in the surface layers. In susceptible areas in southern and central Finland the high level of acidic deposition has reduced the buffering capacity (decrease in pH and base saturation) of the surface soil. The buffering capacity deeper in the soil in such areas is primarily regulated by geological factors such as the particle size distribution of the soil and its minerological composition.

3 PHYSICAL FACTORS OF THE SOIL AND THE CATCHMENT AREA

The bedrock and soil in Finland are composed of silicaceous, sparingly soluble minerals which weather slowly and are thus relatively unable to counteract acidification. The thickness and coarseness of the overburden is of decisive importance. If there is only a thin layer of overburden, the lag time of rainwater is short before it reaches the watercourses. The abundance of coarse, sorted soils also has a similar effect. In addition, the area of contact between the soil particles and water, required by the chemical reactions, is considerably smaller in coarse soils than in fine–grained silt and clay soils.

The study showed that the lakes in exposed bedrock areas in southern Finland were the most acidic, but also that there was an acidification problem in many lakes whose catchment area consisted of compact clay soil, especially if the catchment area was relatively small compared to the surface area of the lake (Nuotio et al. 1990). During peak snowmelt, a small lake or river in such areas is flushed by large amounts of acidic meltwater. Furthermore, the compact soil reduces the formation of groundwater in the area. Sand, gravel and till soils, which are readily permeable to water, neutralize the acidic deposition rather well. This is due to the long lag time of the water in the thick soil layers. As the proportion of groundwater increases, the inflow of water into the lake is more evenly spread out throughout the year and is also more effectively neutralized.

The proportion of surface runoff and percolation in the water flowing out of a forested catchment area was studied using the natural oxygen isotope ^{18}O as a tracer (Lepistö & Seuna 1990). The effects of acidic deposition on meltwater quality were estimated over a short time period (snowmelt episodes) and by examining 20 to 25–year time series.

Percolation accounted for the major portion (70 – 85 %) of the runoff from one forested catchment area also during the flood period. The acidic snowmelt water displaced the water already in the soil into runoff through streams. Only a small proportion of the meltwater flowed directly into the channels, mainly as surface runoff. Water flow right at the beginning of snowmelt was highly concentrated melt–water which leached out the pollutants from the snow, the pH minimum usually occurring later than the meltwater peak. The hydrological conditions explained a considerable part of the variation in the acidity of the runoff water (Lepistö & Seuna, op. cit.).

4 ION BALANCES IN CATCHMENT AREAS

As a result of soil processes, the quality of deposition has already changed considerably by the time it reaches small streams. In principle, the difference between the amounts of ions entering as deposition and those flowing out from a catchment correspond to weathering minus losses through biological fixation. Cation exchange evens out the variation by functioning as an intermediate store of base cations.

Of the nitrogenous compounds, nitrate anions are nutrients that act like bases (e.g. release OH^- when taken up by plants), while ammonium cations in the corresponding situation act like acid (H^+). The considerable role of dry deposition was evident in the budgets. The precipitation collectors underestimated the deposition of gaseous and particulate air pollutants. In particular, sulphur dioxide and dust that accumulates on plant surfaces increase the deposition of many air pollutants by a factor of two compared to the amounts recorded in precipitation collectors in the open (Kallio & Kauppi 1990, Hyvärinen 1990).

An attempt was made to determine which factors affect the acidity of the catchment waters. The processes taking place in the soil were estimated indirectly on the basis of ion balances: the amounts of ions entering the catchment areas via deposition and those removed in water flow were determined. Different processes were compared on the basis of their production or consumption of protons. The material was collected in forested catchment areas in central and southern Finland (Kallio & Kauppi 1990).

Both sulphur and nitrogen deposition especially were bound efficiently in all the catchments (Fig. 3). The absorption of sulphur deposition differed from that observed in southern Scandinavia. The catchment areas of Huhtisuonoja and Myllyoja especially, which contain peatlands, absorbed 60 – 70 % of the sulphate deposition. The inorganic nitrogen compounds in deposition, i.e. nitrate and ammonium nitrogen, were effectively absorbed in the Huhtisuonoja and Myllyoja catchment areas, but on mineral soils in southern Finland about 2 kg of nitrate per hectare were leached out. The leaching of nitrate has also increased in this area during the past couple of decades, and although the amounts leached are still small, they do indicate, in addition to increasing nitrogen deposition levels, that there is a possibility that forest ecosystems are becoming oversaturated with nitrogen (Lepistö & Seuna 1990).

The leaching of bicarbonate (HCO_3^-) was observed in all the experimental areas. This was also evident from the pH values (Yli–Knuutila 6.4, Huhtisuonoja 5.4, and Mylly–oja 5.6). In fact the pH values for Huhtisuonoja and Myllyoja are lower as a result of the humic acids leached from the peatlands. Of the alkali and alkali earth metals (Na, K, Ca, Mg), calcium especially was leached strongly in all the areas. The proportion of leached magnesium out of the input from deposition was, however, much higher.

When the proportions of proton–producing and proton–consuming processes were compared, most (ca. 60 %) of the acidity in the proton budget for Yli–Knuutila (Southern Finland) was derived from deposition. However, reactions involving nitrogen were also of significance (Fig. 4, Kallio & Kauppi 1990). Almost as much acidity was consumed in the weathering of calcium and magnesium and the binding of sulphate. In the Huhtisuonoja catchment area (Southern Finland), which was dominated by peatlands, deposition produced the most acidity, but nitrogen was of no significance. Ammonium is not oxidised to nitrate in acidic, oxygen–deficient peatlands. On the other hand, the absorbance of sulphate bound the most acidity (ca. 65 %). The weathering of alkali earth metals was of less importance.

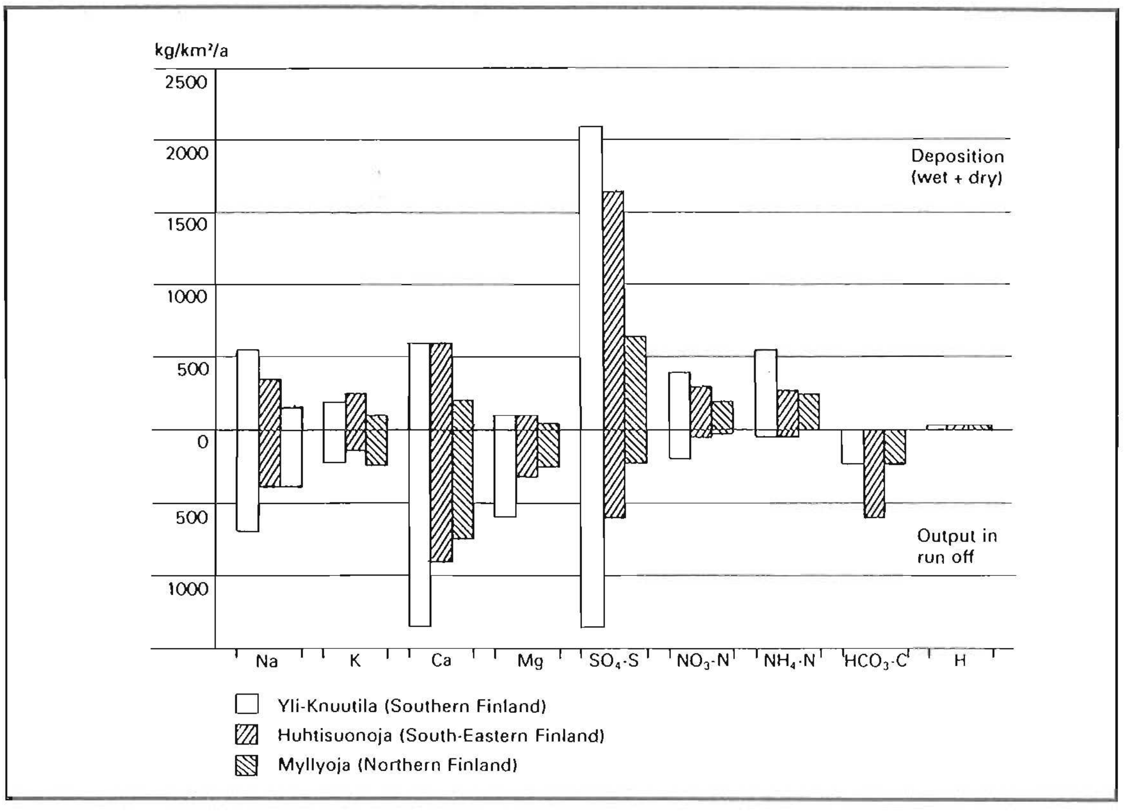

Fig. 3. Ion balances in three forested catchment areas:
1. Yli-Knuutila: High sulphur deposition on mineral soils
2. Huhtisuonoja: High sulphur deposition, 44 % of the area ditched peatland forest
3. Myllyoja: Low sulphur deposition, 27 % of the area peatland

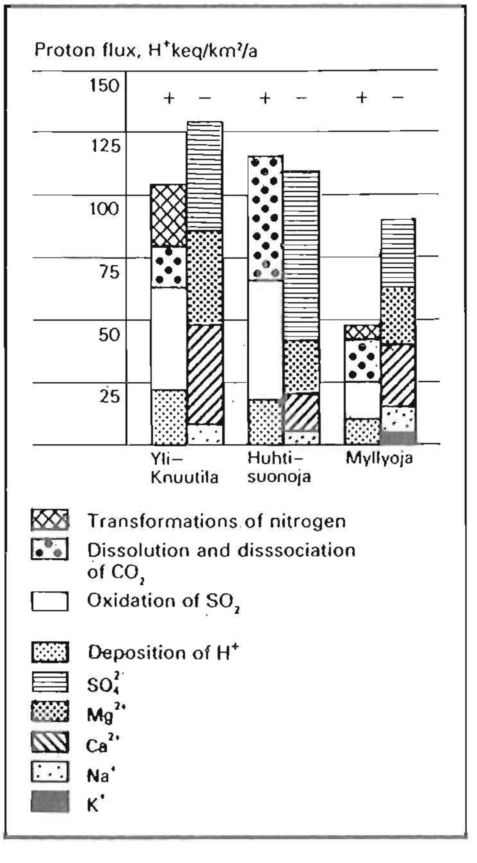

Fig. 4. Acidity status in three catchment areas (Yli-Knuutila, Huhtisuonoja, Myllyoja).

Deposition and leaching were usually the smaller, the further to the north the area was located. The production of protons caused by oxidation and the deposition of sulphur dioxide was greater than the direct deposition of protons. In areas where the proportion of peatlands is high, the proportion of organic acids out of the total production of protons can be as much as half. The proportion of natural acidification in some areas is thus still significant. Sulphate was absorbed by the soil in all the areas. Nitrogen may also be of importance from the point of view of surface water acidification in southern Finland (Kallio & Kauppi, op. cit.).

5 THE ACIDITY OF WATERCOURSES IN FINLAND

The area of lakes in Finland is ca. 32 000 km^2, of agricultural land ca. 26 000 km^2 and of forest land ca. 210 000 km^2. An abundance of both large lake networks and small forest lakes is characteristic of Finland. The proportion of large lakes (> 10 km^2) out of the total area of lakes is ca. 64 %. In addition to these 300 large lakes, there are about 55 000 smaller (> 1 ha) and 132 000 small (< 1 ha) lakes.

5.1 Acidification status of the main watercourses

During the 1970's the cation concentration of the large lakes increased by ca. 9.5% and the measured anion concentration by only 2.1 %. The only measured anion whose concentration fell was bicarbonate (alkalinity). This rather worrying trend from the point of view of acidification was recorded at as many as three quarters of the observation points. The dominating proportion of sulphate out of anions increased from 52 to 65 % in the monitored lakes (Laaksonen & Malin 1984).

The quality of the water in large lakes has been monitored since the beginning of the 1960's. A statistically significant decreasing trend in alkalinity has been observed in only a few lakes, and none of the lakes are acidic, i.e. they still all contain alkalinity.

Sewage discharge and agriculture, which in practice increase alkalinity, have a strong effect on the water quality of large rivers. However, comparison of old (1911–1931) and new (1962–1979) monitoring data showed that the alkalinity of samples taken in the spring has clearly decreased over time (Alasaarela & Heinonen 1984).

5.2 The acidity of small lakes

According to studies carried out in a number of countries, acidification is primarily a problem of small forest and mountain lakes and streams. Preliminary studies based on material for about 8 000 lakes in the Water Quality Register of the National Board of Waters and the Environment showed that ca. 6 – 7 % of the lakes were acidic. However, three quarters of the acidic lakes were brownwater humus lakes, whose acidity is presumably due to the presence of organic acids (Forsius et al. 1987). Because a fully compatible material was considered to be necessary, about 1 000 lakes, based on a statistical random selection of small lakes, were sampled in autumn 1987 (Forsius et al. 1990). All the necessary analyses pertaining to acidification were carried out so that the results could be compared e.g. to the corresponding study carried out in Norway. The lake cohort corresponded to about 2 % of all lakes in Finland with a size of 0.01 - 10 km^2. In northern Finland, however, lakes < 0.1 km^2 were not included, but instead 5 % of all the 0.1 - 10 km^2 lakes. Every analysed lake thus represented 50 lakes, and the study gives a representative picture of the whole country.

According to this survey, there are assumed to be ca. 4 900 lakes without any buffering capacity (alkalinity < 0 $\mu eq\ l^{-1}$) in Finland. Acidic lakes are to be found throughout almost the whole country. Over 50 % of the acidic lakes (pH < 5.3) were presumably naturally acidic humic lakes. The greatest number of lakes clearly classified as acidified occurred in southern Finland (Fig. 5).

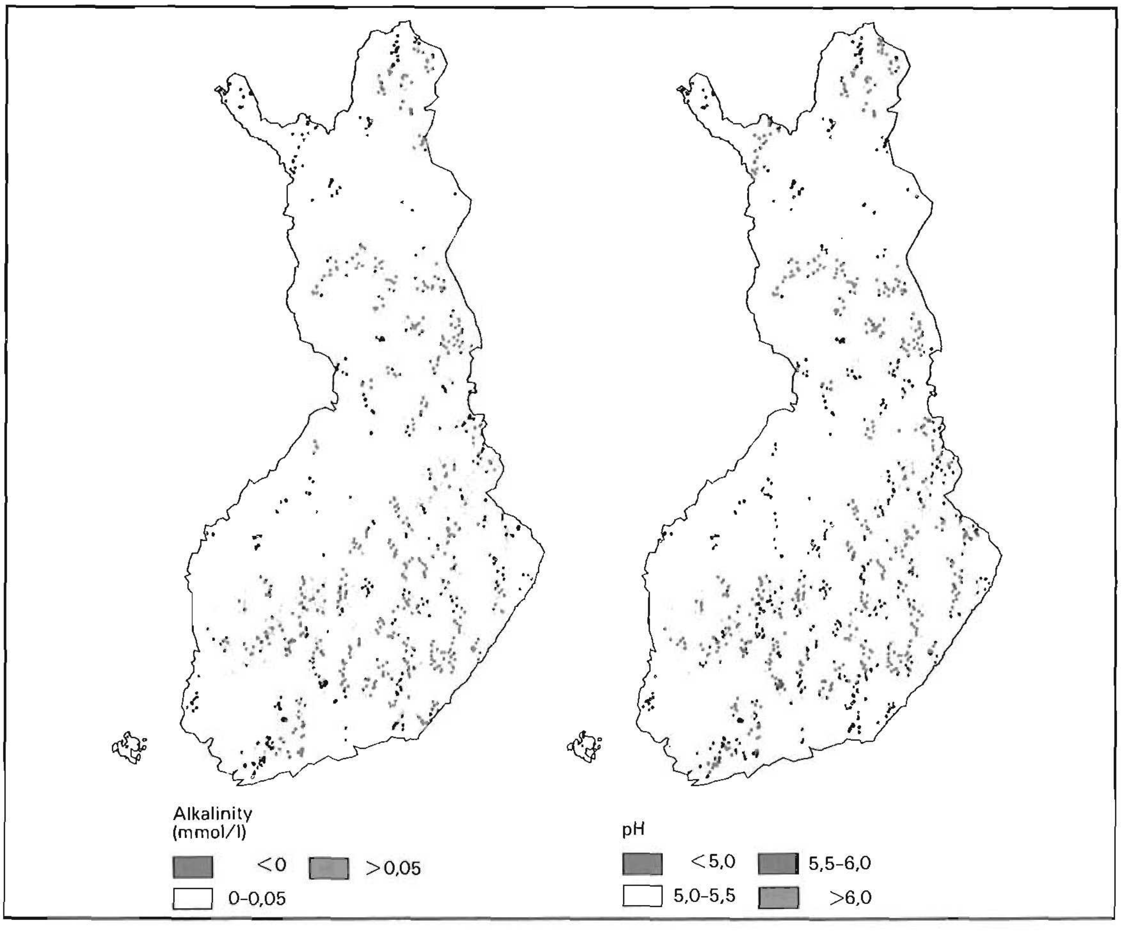

Fig. 5. Distribution of alkalinity and pH in autumn 1987 according to a survey carried out in 987 small lakes.

The ionic ratios of the lakes showed that the major anion in the southern parts of the country was organic anions (humic substances), only slightly exceeding the proportion of sulphate (Fig. 6). Bicarbonate, determined in the alkalinity analyses, held third place. On the other hand, the major anion in northern Finland was bicarbonate, the second largest organic anions, and the third sulphate. Of the cations, the ratios between alkaline-earth metals (Ca and Mg) and alkali metals (Na and K) were approximately the same in both regions. The hydrogen ion concentration, i.e. acidity, was clearly higher in the southern half of the country. In northern Finland the lakes were almost neutral and rather well buffered. Their overall electrolyte concentration was, however, clearly smaller than that in the lakes in the south.

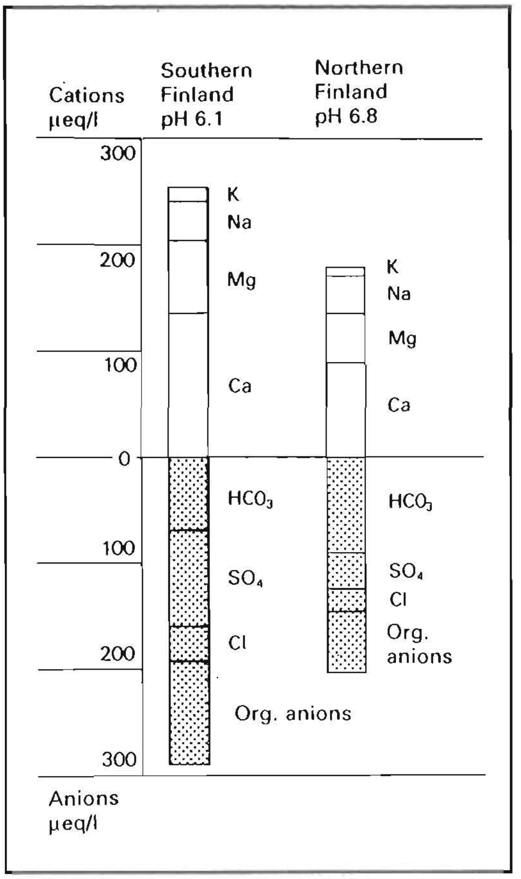

Fig. 6. Major ions in lake water according to a survey carried out in 987 small lakes.

The proportion of nitrate out of total anions in the waters was very small even in the southern part of the country, and in the north almost undetectable. This indicates that nitric acid is of no importance as a water–acidifying factor, and that organic acids and sulphuric acid determine the acidity level in Finland. The sulphate concentration in the southernmost lakes was almost triple that in lakes in northern Finland. The higher sulphur deposition level in the south well explains this finding. The deposition of base cations is also higher in southern Finland, but the lower levels in the northern lakes of Finland may also be due to geological and hydrological reasons.

5.3 Organic acidity in lakes in Finland

Forested and boggy terrain produce large amounts of organic matter. This explains why high concentrations of organic matter is one of the most prominent features of surface waters in Finland.

The lake survey (Forsius et al. 1990) indicated high total organic carbon (TOC) concentrations throughout the southern and central parts of the country. Small headwater lakes with a large catchment area and drainage from peaty soils had the highest concentrations. The lower TOC concentrations in northern Finland are mainly due to the colder climate and subsequently lower primary production. The median TOC concentration in the full data set was 12 mg l^{-1}, and the median pH 6.3. The proportion of lakes with TOC concentrations higher than 5 mg l^{-1} was 91 % in the whole country.

Organic humic matter strongly affects the acidity of lakes in Finland. The pH–lowering effect of organic matter was demonstrated by both regression analysis and ion–balance calculations. Organic anions, estimated by ion–balance calculations (organic anions = $Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + H^{+} + NH_4^{+} + Al^{3+} - SO4^{2-} - Cl^{-} - NO_3^{-} - F^{-} - HCO_3^{-}$), were the main anion (median 89 μeq l^{-1}) in the full data set (Kortelainen & Mannio 1990).

Organic anions dominated in acidic lakes, indicating that a substantial proportion of the overall acidity of such lakes was of natural origin (Fig. 7). When the lakes were grouped by pH class at 0.5 pH unit intervals, organic anions were the dominant anion in the average lakes in all subgroups below pH 6.5. The contribution of sulphate also increased with decreasing pH, and minerogenic acidity frequently exceeded organic acidity in areas of southern Finland with high sulphur deposition (Kortelainen et al. 1989).

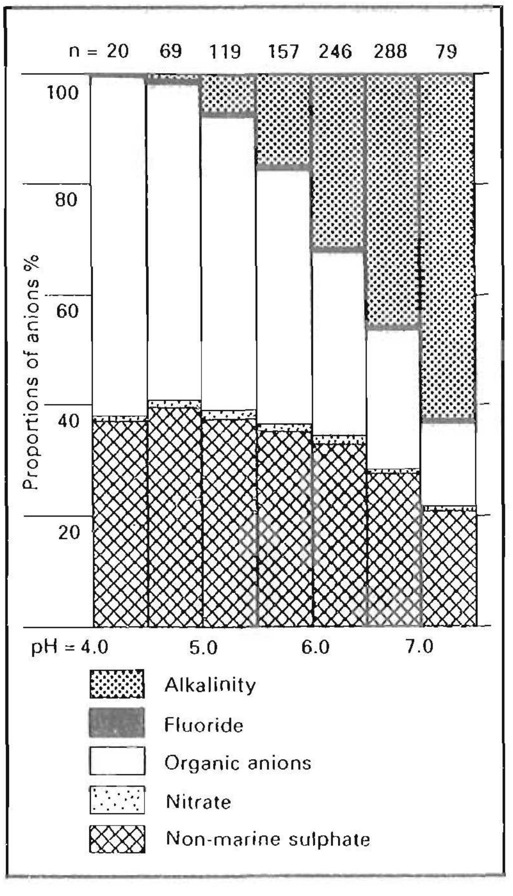

Fig. 7. Percentage of main anions in different pH-classes of small lakes in Finland (modified from Kortelainen et al. 1989).

6 ACIDIFICATION AND THE HEAVY METAL LOAD OF WATERCOURSES

The effects of the atmospheric deposition load and watercourse acidification on heavy metal concentrations in lake sediments, water and organisms throughout the whole country were investigated in the study (Verta et al. 1990). The points of study were small, headwater forest lakes not subjected to sewage inputs.

The regular monitoring of heavy metals is rather new in Finland. On the other hand, the monitoring of heavy metal concentrations in snow was began as early as 1975. Snow acts as an accumulative deposition collector, and it is also possible to estimate the annual rate of deposition from the water content of the snow and duration of the snow cover. Heavy metal concentrations in southern and northern Finland (below and above latitude 62°) are presented as an example in Table 1.

The current low concentrations of heavy metals in water are not directly harmful to either aquatic organisms or to humans. The ratios between heavy metal concentrations in the 5-cm-thick uppermost sediment layer (representing the last few decades) and the 18 to 30-cm-thick sediment layer (the preindustrial era) are shown in Table 2.

Table 1. Mean heavy metal concentrations ($\mu g\ l^{-1}$) of snow samples and lake water in southern and northern Finland (Verta et al. 1990).

	Southern Finland		Northern Finland	
	Snow	Lake	Snow	Lake
Lead (Pb)	4.8	0.12	2.2	0.12
Zinc (Zn)	6.9	5.6	4.5	2.5
Copper (Cu)	2.0	0.38	0.86	0.43
Nickel (Ni)	1.6	0.4	0.45	0.25
Cadmium (Cd)	0.07	0.03	0.04	0.02

Table 2. The enrichment factor (= maximum concentration in surface sediments/mean concentration in deep sediments) of some metals in lake sediments in Finland (Verta et al. 1990).

	Enrichment factor	
	Southern Finland	Central and Northern Finland
Lead (Pb)	17.8	14.4
Zinc (Zn)	6.2	2.0
Copper (Cu)	1.9	1.7
Nickel (Ni)	1.7	1.3
Cadmium (Cd)	8.1	4.8

A ratio value of > 1.0 indicates an increase in metal deposition on lakes. If the differences between the rate of accumulation of heavy metals in the surface sediment and that in preindustrial sediment are considered to be attributable to anthropogenic activities alone, then the proportion caused by man is nowadays 60 – 95 % for Cd, Hg and Pb of the total load on forest lakes in southern and central Finland. The proportion for Zn was 40 – 90 %, and the variation in Ni and Cu was the greatest (0 – 84 %). The concentrations of Al, Mn, Zn, Pb and Cd were higher in general in acidic lakes. Acidification increased the accumulation of Pb, Cd and Hg in bottom invertebrates, aquatic plants and fish. The Pb concentrations in the bones of the fish exceeded by a factor of as much as 100 the levels in fish from neutral lakes (Fig. 8).

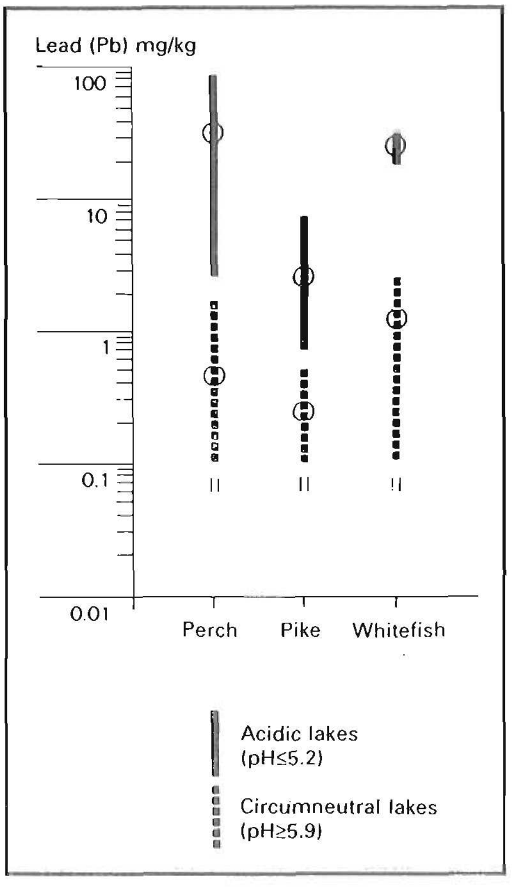

Fig. 8. Lead concentration in perch, pike and whitewfish bones in acidic (pH < 5.3) and more neutral (pH > 5.9) lakes.

The increased heavy metal concentrations in the sediments of the forest lakes were explained by the atmospheric pollution load. Inorganic Al occurs in acidic lakes at concentrations that disturb fish reproduction. Acidic conditions affect the heavy metal concentrations in fish, aquatic plants and some bottom invertebrates more than the metal load on the lake (Verta et al. 1990).

7 ACIDIFICATION OF GROUNDWATER

In Finland the groundwater reserves are mainly replenished following spring melt and, to a smaller extent, also in autumn. The quality of the meltwater that eventually becomes groundwater is obtained from snow samples taken before the onset of spring melt. When the monthly deposition measured from precipitation collectors and that calculated on the basis of the snowmelt water were compared, the sulphate and nitrate deposition values given by both methods were almost the same, but the deposition of base cations was clearly higher in snow (Soveri & Ahlberg 1990).

Groundwater quality is decisively affected by the chemical reactions that take place between the water and soil in different soil horizons as the water moves down from the surface to the groundwater.

The chemical composition of the meltwater changes as it percolates down through the soil. The processes responsible for these changes were investigated using gutters, located at different depths, that led the water off into collection vessels. The results obtained as averages for three depths (immediately below the humus layer, 0.25 m and 0.55 m) at three locations during the three-year monitoring period showed that the composition of snowmelt changed rather rapidly as it percolated down through the soil (Fig. 9). Water acidity decreased by about one pH unit, and the ammonium and nitrate concentrations also decreased. In contrast, the base cation concentrations increased, and that of sulphate increased by as much as fourfold. The aluminium and iron concentrations increased immediately below the humus layer, but decreased on moving deeper into the soil. Most of the iron and aluminium was thus retained in the enrichment layer of the podzol profile because the dissolution of base cations increased the pH and alkalinity.

Groundwater quality has been monitored since 1975 in monitoring areas of the National Board of Waters and the Environment. No significant changes have taken place in the acidity or alkalinity status of the groundwater. On the other hand, the sulphate and nitrate concentrations have increased in many areas in southern and central Finland (Fig. 10).

The main reason for the increase in the ionic concentrations of groundwater is the atmospheric load of sulphate and nitrate. So far, the buffering capacity of the soil has been able to counteract a decrease in pH and alkalinity in the groundwater (Soveri & Ahlberg 1990).

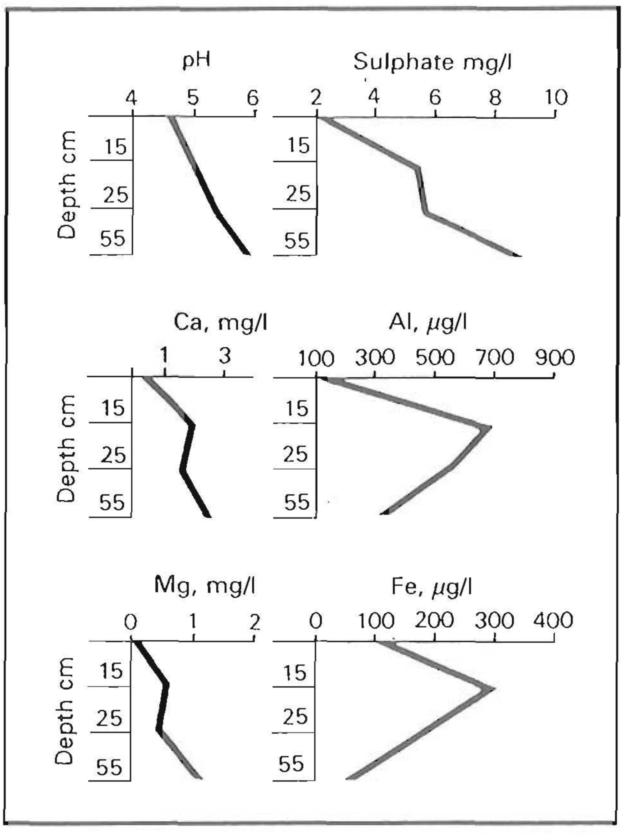

Fig. 9. Change in the properties of snowmelt water percolating down through the soil at three different depths. The experiment was performed using lysimeters during 1986 - 1988.

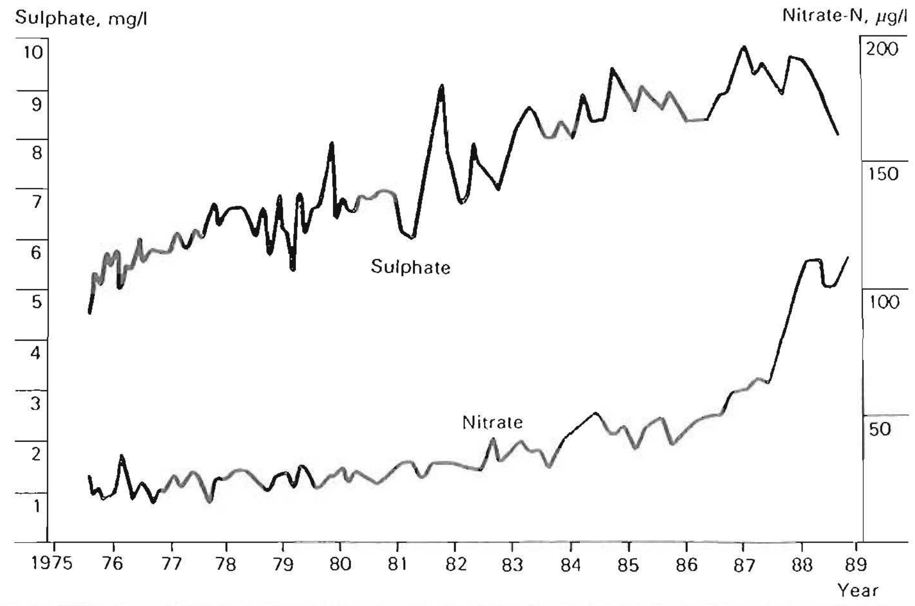

Fig. 10. Sulphate and nitrate concentrations in groundwater samples collected at Karkkila in southern Finland during 1975 – 1988.

8 THE EFFECTS OF ACIDIFICATION ON LAKE AND STREAM BIOTA

The detrimental effects of acidic precipitation in lakes and streams are centred on its biological effects. In fact, the disappearance of fish stocks in southern Norway was one of the most important findings in the history of acidic rain research. Nowadays, most national and international efforts against air pollution have been directed at protecting natural ecosystems, both aquatic and terrestrial.

Finnish research on the effects of acidification on aquatic ecosystems began as early as 1984. The preliminary report dealt only with the macrophyte, bottom fauna and zooplankton in 55 small forest lakes (Kenttämies et al. 1985). During 1985–1988 the Finnish Acidification Research Project (HAPRO) continued the biological water re-search programme so that all the main organism groups and habitats have been included in the study.

The first aim of this research was to study the effects of acidity on the biota of small lakes in Finland. Regional acidification studies on lake biota are not very common. In this study the chosen lake set was considered to represent the acid-sensitive and small headwater lakes north of latitude 60° in areas with granitic bedrock and thin soils.

The second aim was to develop biological indicator methods for use, together with chemical methods, in practical surveys of lake acidity. Simple and fast methods are needed for evaluating the acidity of a lake for e.g. local fisheries and determining the liming requirement. The third aim was to evaluate the biological methods for monito-ring the acidification of lakes and streams.

For the integrated geological, limnological and biological studies, a group of 140 lakes was selected to represent acidic-sensitive, small lakes. The lakes were principally headwater forest lakes in southern and central Finland. The biological survey of the lakes was carried out during 1984 - 1986. The samples were taken only once, in July-August. The sampling included phytoplankton, zooplankton, littoral periphyton, deep surface sediment, zoobenthos and macrophytes. The mapping of macrophytic vegetation was carried out simultaneously. The methods have been presented in detail by Kippo-Edlund & Heitto (1990) (phytoplankton), Sarvala & Halsinaho (1990) (zooplankton), Eloranta (1990) (periphyton), Huttunen & Turkia (1990) (sediment diatoms), Meriläinen & Hynynen (1990) (zoobenthos) and Heitto (1990) (macrophytes).

8.1 Macrophytes

The few macrophyte species in acidic (pH < 5.4) lakes mainly consisted of floating-leaf, aquatic plants (e.g. yellow water lily (*Nuphar luteum*)) and aquatic mosses (e.g. *Sphagnum*), and in clear, sandy bottom lakes also isoetids (e.g. quillwort (*Isoetes lacustris*)).

Most submerged-leaf (elodeid), aquatic plants (e.g. *Myriophyllum sp.*) were completely absent. The number of species in almost all biotype groups was clearly greater in lakes with pH values close to neutral than in acidic lakes (Fig. 11). Aquatic mosses were the only group with more species in acidic lakes (Heitto 1990).

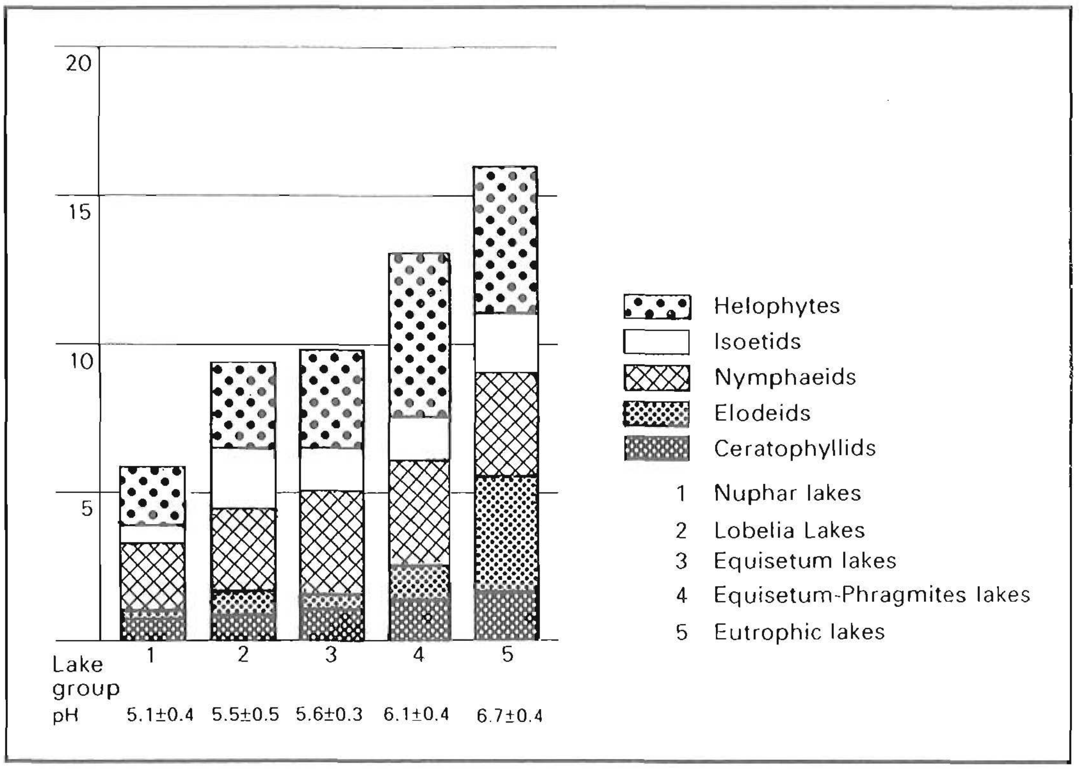

Fig. 11. Number of species and groups of aquatic plants in lake types defined according to different acidity classes.

The aquatic flora in oligotrophic forest lakes susceptible to acidification mainly comprised species whose highly developed root systems enable them to obtain most of their nutrients from the bottom sediment. Changes in water quality are thus not rapidly reflected in the floristic composition. Although elodeids are, owing to their less-developed root systems, more sensitive to changes in water quality, they do not usually occur naturally in such lakes. Aquatic mosses benefit from acidification and their multiplication brings about considerable changes in the ecosystems of small lakes.

8.2 Phytoplankton

The composition of phytoplankton communities well reflects the acidity status of waters. Different algal species have different pH optima, and hence the species composition matches the acidity level. The following taxa were typical of the acid lakes: *Peridinium inconspicum, Peridinium sp., Gymnodinium sp., Oocystis borgei, Monoraphidium minutum, Chlamydomonas sp., Dinobryon pediforme and Dinobryon sp.* (Kippo-Edlund & Heitto 1990). Because watercourses sensitive to acidification are oligotrophic, mineral plant nutrients were of little importance in this material. The acidity and humic concentration were more important factors affecting the composition of the phytoplankton flora. Dinoflagellates and chrysophytes were dominant in clear-water, acidic lakes (Fig. 12), while cryptophytes were common in humic-rich lakes. Cryptophytes were also dominant in brown-water lakes with a pH close to neutral, while other groups of algae, such as green algae, grew better in more alkaline, clear-water lakes. Although the results suggested that water colour has an effect on total phytoplankton biomass and the biomasses of the different algal groups in acidic lakes, the main determinant of species composition may nevertheless be pH (Kippo-Edlund & Heitto, op. cit.).

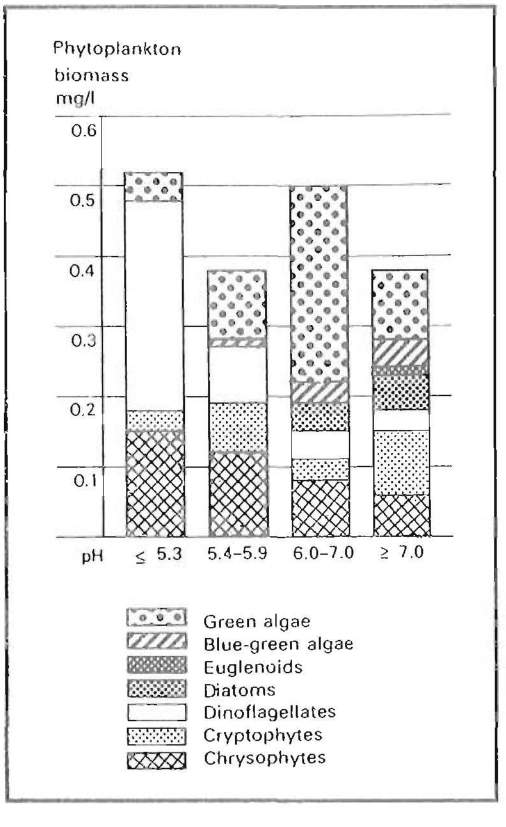

Fig. 12. Distribution of phytoplankton biomass in different algae groups in clear-water lakes of different acidity class.

8.3 Periphytic diatoms and lake acidity

In the littoral zone, microscopic algae are to be found unattached on the surface of the sediment, attached to the surface of a range of substrates, and, of course, in the form of free–floating plankton in the same way as in the open water. The periphytic algal species attached to substrates mainly consist of filamentous algae and diatoms belonging to a wide range of groups. Because rather a lot is known about the environmental requirements of diatoms, especially the diatoms in the periphytic algal group, are good indicators of the conditions prevailing in their habitat. The structure and species number of periphytic algae were examined in the study in relation to water quality characteristics and especially water pH (Eloranta 1990).

The number of periphytic algal species is greater at higher pH values. A total of 135 lakes were divided into 8 groups on the basis of water quality and structure of the diatom assemblages. The groups differed from each other especially with respect to water pH and COD (depicting the organic matter concentration) and electrical conductivity. The diatom communities in the groups differed from each other with respect to the relative proportions of species belonging to the different acidity classes, as well as with regards to species number. Six lake classes were formed according to the COD and alkalinity of the water. Those lakes where the alkalinity was < 0 meq l^{-1} and the COD value < 5 mg l^{-1} had the highest number of acidic water species. On the other hand, the total number of species in this group was the lowest. The number of species that indicate neutral water was significantly higher and the number of species that indicate acidic water was smaller in all those COD groups where the alkalinity was > 0 meq l^{-1} (Eloranta 1990).

The prevailing acidic conditions can be well depicted using the periphytic algal community. The community in the littoral zone can also be used to indicate differences in the water flowing in from the immediate catchment area and differences between the quality of water in the littoral zone and in the open water. It is easier to use the littoral zone community in routine monitoring than, for instance, communities from the surface of deep water sediments owing to the ease of sampling. Interpreting the results for littoral algae is easier than that of bottom sediments because the latter is a mixture of communities of different age and origin (Eloranta, op. cit.).

8.4 Surface sediment diatoms and lake acidity

Counting methods based on the diatom assemblages used in lake acidification research were compared in the study. According to the results of canonical correspondence analysis (CCA), the structure of diatom assemblages correlates closely with the pH and pH–related factors of lake water (Huttunen & Turkia 1990). Hustedt's classification of diatoms seems to reflect fairly well the pH status. Acidobiontic diatom taxa, for example, clearly indicate acidic conditions. According to the results obtained using the weighted averaging method, however, some diatom species classified as acidophilous can tolerate low pH conditions to an equal degree. As regards pH–indicator methods based on diatom assemblages, pH was predicted more precisely by canonical correspondence analysis and by weighted averaging based on the optimum and tolerance of species, than by multiple regression or the diatom indices.

The most reliable method for predicting acidity proved to be the diatom frequency-based approach that is based on weighted means calculated from environmental factors for each species. It predicted lake water pH to an accuracy of ± 0.16 pH units.

Planktic diatoms were almost completely lacking from acidic but clear-water lakes. The species composition in dark-coloured, humic lakes, which are the most typical type of forest lake in Finland, differed from that of acidic, clear-water lakes. This feature should be taken into account when applying the bioindicator method. The results showed that the method based on diatom assemblages is applicable in acidification monitoring research. The method can be used to estimate changes in lake acidity and buffering capacity both in the short and in the long term without having to resort to continuous water quality monitoring.

Two biological pH meters, based on the different acidity tolerance of diatom species, were subsequently developed in the research programme (Eloranta 1990, Huttunen & Turkia 1990). Compared to measurements made on water samples, these methods have both advantages and disadvantages. The main advantage is that the diatoms depict the typical acidity conditions prevailing over long periods (minimum of one year), while chemical measurement represents only the situation at the sampling instant.

pH determination using diatoms is well suited for survey studies in which comparative acidity data, free from momentary variation, is required. As a biological method, the deviation of "diatom pH" is rather large, and thus cannot compete with an ordinary pH meter.

8.5 Crustacean zooplankton and lake acidity

Zooplankton is an important trophic link between phyto- and bacterioplankton and fish. The most valuable fish species in lake fisheries in Finland - vendace and whitefish - are planktivorous, and the young of most other species rely heavily on zooplankton food during their first summer.

The composition of zooplankton in forest lakes in Finland, and its relationship to water acidity and 23 other physical and chemical environmental factors, were studied in "one-off" samples from 138 lakes using statistical methods (Sarvala & Halsinaho 1990).

Zooplankton were most abundant in shallow lakes. Their numbers increased along with an increase in nutrients and phytoplankton biomass, water colour and organic carbon and calcium concentration. The number of crustacean zooplankton species and individual densities decreased with increasing acidity and decreasing buffering capacity; the change was especially prominent in the case of *Eudiaptomus, Heterocope* and *Daphnia* species. The reduction was greatest in the most acidic lake class (pH < 5.2). A relatively high humus concentration clearly alleviated the adverse effects of acidity. The number of species detected was also dependent on sample size.

Although the effects of acidity and certain other water quality parameters were statistically significant, they explained only a very small proportion of the variation in zooplankton between the lakes. Acidification primarily affects zooplankton via biological interactions, e.g. through nutrition (phyto– and bacterioplankton) and predators (fish and invertebrates).

8.6 Benthic invertebrates and lake acidity

The relationship between lakewater acidity and benthic invertebrates was investigated in 140 forest lakes where the acidity varied from pH 4.3 – 7.3. The suitability of using benthic invertebrates as indicators of acidification trends was also elucidated.

The number of benthic invertebrate species decreased with increasing acidity. However, species resistant to acidity may occur in very large numbers in acidic waters. The biomass and number of animals was not correlated with lake acidity (Meriläinen & Hynynen 1990).

Snails, a number of mayfly species and *Pisidium* snails were more sensitive, and the number of species started to decrease as the pH fell below 6. No snail species were found in lakes with a pH below 5.3. Large insect larvae, dragonflies, alderflies and caddisflies and the chironomid group covering a large number of species, were the most tolerant of acidic lake water. The effect of acidity was clearest in the animals of the littoral zone. The number of benthic invertebrates in deep parts of the forest lakes were small due to the poor oxygen conditions. Deep–water species that tolerate the low oxygen concentrations are usually also insensitive to acidity. It is therefore difficult to demonstrate the effects of acidification unless the development of the fauna in the deep parts of lakes is known over a longer period (Meriläinen & Hynynen, op. cit.).

The benthic invertebrates in the littoral zone of lakes provide information about the degree of acidification of the lake and can be used to monitor acidification trends. Changes in the fauna depict the direct and immediate changes caused by acidification, and also the indirect, changing competition and food conditions.

8.7 Benthic invertebrates and stream acidity

The effects of acidification are likely to become first apparent in streams and brooks where the rainwater temporarily constitutes a high proportion of the water volume. The annual minimum pH usually occurs in the spring when the melting of the snowpack, containing the accumulated acid load, takes place.

The distribution of benthic invertebrates was studied in relation to stream acidity. Of the two methods applied, the first was the tolerance limit (TL) method based on the presence/absence of indicator species. The second method involved the weighted averaging method based on species optima and tolerances. These were estimated by maximum likelihood (ML) and weighted averaging (WA) methods, assuming unimodal relationships between the relative abundance of invertebrate taxa and stream pH (Hämäläinen & Huttunen 1990).

The total number of taxa increased with increasing stream pH. Within the same pH range, the number of taxa appeared to be higher in humic versus clearwater streams.

At the species level, the distribution of *Baetis* mayflies also indicated that humic substances may alleviate the harmful effects of low pH. According to the tolerance limits, few highly acid–sensitive taxa were found, but differences in stream acidity could be demonstrated by observing the appearance of species with different sensitivities. The minimum pH predicted from both the ML and WA estimates showed a highly significant correlation with the observed stream pH. The results suggest that the pH in lake surface water during the spring snowmelt period can also be assessed by the use of outlet invertebrate assemblages. The results do not reveal the order of superiority of the two methods in detecting acidity level. The method of weighted averaging was, however, considered more informative in monitoring acidification (Hämäläinen & Huttunen, op. cit.).

Many foreign studies have demonstrated that benthic invertebrates are good indicators of acidification in lakes and rivers. Their applicability is based on the fact that many species are sufficiently long–lived for the year–round estimation of watercourse condition. The presence of acidity–sensitive species can predict the lowest probable pH level, as long as sufficient reliable information is first obtained about the acidity tolerance of the species.

8.8 The effects of acidification on fish

The effects on fish and their development, especially threatened fish and crayfish stock, and, to some extent, the prevention of these detrimental effects, were investigated in acidified areas as part of the HAPRO Project. Considerable emphasis was placed on the application of basic research concerning the acidity tolerance of fish species to Finnish conditions.

In investigations concerning the effects of acidity and aluminium on the activity of the reproductive organs of whitefish (*Coregonus wartmanni* sensu Svärdson 1979), aquarium experiments showed that spawning maturity, i.e. ovulation readiness, was delayed (Vuorinen et al. 1990). Thus the spawning behaviour of females was also delayed. In turn, the regression of testes in males after spawning slowed down to the extent that the milt was still fluid even a few weeks after spawning. The spawning readiness of whitefish and perch was also found to be delayed by as much as one month in an acidified lake where the aluminium concentration was fairly high. The delay in spawning resulted, in addition to a shorter growing season for the fry during the first summer, in disturbances in embryo development.

Fertilization of fish eggs succeeds to some extent in rather acidic water, usually down to pH 4. However, the fertilization percentage was found to fall, in the case of migrant whitefish, at pH 5 (Vuorinen et al., op. cit.). No clear differences were found over the acidity range pH 6.7 – 4.0 in experiments where spawn and milt were kept either in acidic water alone or in acidic water containing aluminium for one minute, allowing sufficient time for fertilization to take place. Swelling of the eggs following fertilization was disturbed in acidic water containing aluminium. The growing space for the embryo, the perivitelline space, was thus smaller than normal in the eggs of whitefish. It has been shown that, after the initial stage in embryo development, spawn mortality remains low even in acidic water and increases again sharply after the fry hatch. The tests on pike, roach, bream and whitefish, which continued throughout embryo development and hatching, showed that roach is exceptionally sensitive. Embryo development in roach was unsuccessful over the pH range 5.0 – 5.25, but pike spawn developed into living fry even when the pH was one unit more acidic.

The fry stage, following hatching of the eggs, has been shown to be critical for survival of the fish stock. Lethal dose tests (LD) clearly demonstrated the relative differences in sensitivity of different species of fish, and also gave hints for the ecological estimation of the acidity tolerance of fish stocks (Fig. 13). Pike fry were the most resistant to acidity and aluminium, young roach the least. Whitefish was also rather resistant. Aluminium accentuates the detrimental effects of acidity or, vice versa, acidity the toxicity of aluminium (Tuunainen et al. 1991).

Part B of Fig. 13, which includes non-motive fry as well as dead fry, gives perhaps the most realistic overall picture of toxicity in nature, where inactivation may at the same time mean death.

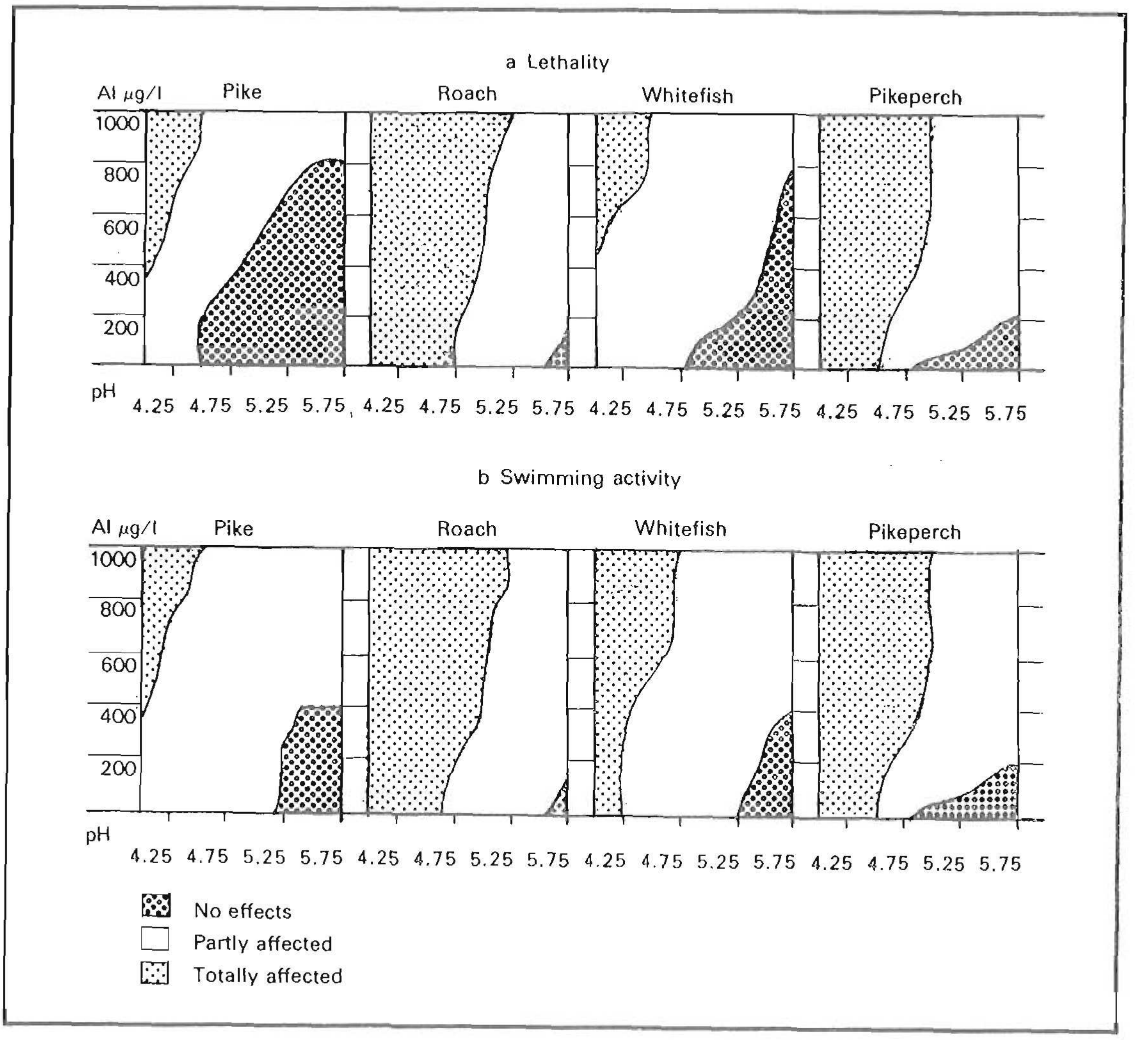

Fig. 13. Effect of acidity and aluminium concentration on the fry of perch (Perca fluviatilis L.), roach (Rutilus rutilus), whitefish (Coreconus pallasi Valeciennes) and pikeperch (Stizostedion lucioperca) on the basis of lethality (A) and swimming activity (B). The fry were exposed for ten days to acidity and aluminium in solutions made up using lake water (Ca about 4.6 g l^{-1}). (Modified from Tuunainen et al. 1991).

The order of sensitivity of the fish species, based on fry mortality, was:

roach (*Rutilus rutilus*) >
pikeperch (*Stizostedion lucioperca*) >
whitefish (*Coregonus pallasi Valenciennes*),
perch (*Perca fluviatilis*) >
pike (*Esox lucius*)

In addition to the differences in tolerance between the species, different stocks also differed from each other. In the experiments, perch fry from acidic lakes resisted acidity better than the fry of females that had lived in a nearly neutral lake (Tuunainen et al. op. cit.).

Acidic water in combination with high aluminium concentrations resulted in the swelling of the gill lamellae and increased mucus secretion. This may result in problems in the diffusion of oxygen from the water into the fish. The fish suffer from oxygen starvation and try to stay alive by vigorously hyperventilating. In addition, the leakage of excess sodium and chloride ions from the blood plasma into the water induces the same symptoms. In studies carried out by the Zoological Institute, University of Helsinki, water with a low oxygen content was found to further increase the leakage of ions from the plasma (Nikinmaa et al. 1990). This may be of ecological importance because a shortage of oxygen, caused especially by biological oxygen consumption by humus substances, is a typical condition in small lakes in Finland.

Natural fish reared in acidic water did not exhibit any such structural damage to their gills as in laboratory exposure experiments. However, the external surface of chloride cells in the gills had become wrinkled. In contrast, the blood haemoglobin level of the fish was higher in an acidic lake. This indicates some kind of physiological response caused by oxygen starvation of the blood (Nikinmaa et al., op. cit.).

A study carried out by the Game and Fisheries Research Institute showed that atmospheric load derived acidification in Finland has not resulted in a situation corresponding to that in southern Scandinavia. Studies carried out on the fish stocks of 80 mainly acidic or acidic-sensitive lakes showed that there are only a few fishless, acidified lakes in southern Finland. On the other hand, a large number of less severe structural changes were found in fish stocks that are characteristic of acidification (Rask & Tuunainen 1990).

Large mean fish size is characteristic of fish stocks in the critical stage of extinction. The stocks consist of only a few old fish (Fig. 14). The stocks have presumably not been able to reproduce owing to the failure of spawning caused by water acidity or death of the fry. Continuous failure to reproduce naturally results in the disappearance of the whole stock. The complete death of spawn in the most acidic lakes was observed in the studies. An exceptional observation was also the death of adult fish immediately after spawning (Tuunainen et al. 1991).

A statistical survey of the chemical composition of small lakes (Forsius et al. 1990) and the information obtained in research about the tolerance of perch and roach make it possible to estimate the total number of disturbed stocks in the whole country. An estimated 13 – 26 % of those lakes whose pH was below 5.3 was used as the proportion of anthropogenically acidified lakes because most of the acidic small lakes have become acidified as a result of the humic substances derived from peatlands. Perch was assumed to occur in all these lakes, but roach in only 61 % of those lakes whose pH is over 5.8. Atmospheric acidification has thus affected the structure of the roach stocks in 780 – 1560 lakes south of latitude 66°, and wiped out the stocks in 330 – 670 lakes. Correspondingly, the perch stocks would have changed in 110 – 220 lakes and been wiped out in 12 – 24 lakes. If it is assumed, in the absence of research results, that pike and ruff stocks behave in the same way as perch, and add on the effects on other Cyprids, burbot, whitefish and vendace, then we can estimate that atmospheric acidification has affected 1000 – 2000 fish stocks and wiped out 500 – 1000 (Tuunainen et al. 1991).

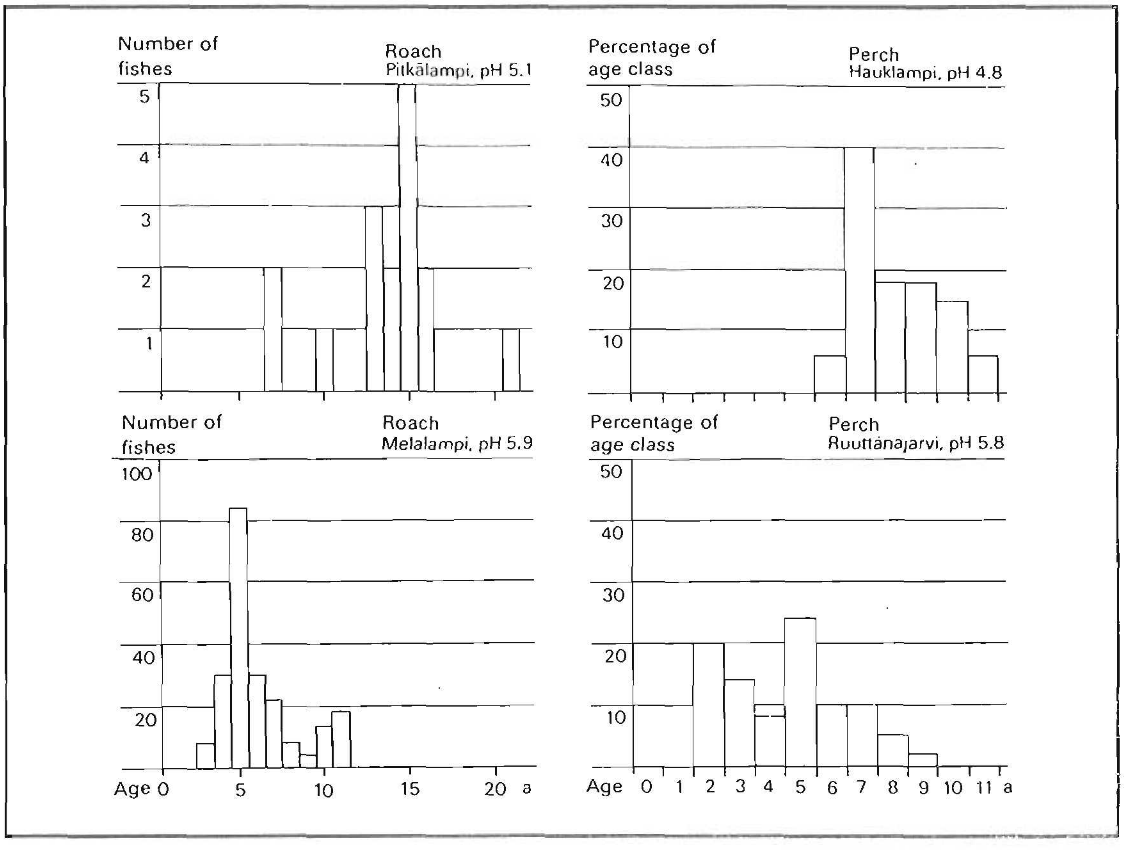

Fig. 14. Age distribution of perch and roach stocks in acidic and neutral lakes. (Modified from Tuunainen et al. 1991).

8.9 Crayfish and water acidification

The crayfish (*Astacus astacus*) is economically very important in Finland. The value of crayfish catches in small watercourses especially is usually many times that of the fish catch. Crayfish are also very sensitive to acidification and, furthermore, the crayfish stocks are affected by many diseases, especially the crayfish plague caused by the mold *Aphanomyces astaci*.

The small lakes and streams in the upper parts of catchment areas have come to be the last habitats of the crayfish in southern Finland as the plague has gradually spread through the main watercourses. The effect of acidification on crayfish populations is such that, in the initial stages, reproduction is disturbed and prevented. The female crayfish carry the fertilized spawn, produced in the autumn, right up until midsummer the following year. The spawn is attached to the underside of the tail by means of a mucous secretion. The development of crayfish was followed in experiments carried out by the Game and Fisheries Research Institute in which females were kept in cages in acidic lakes. Successful incubation of the spawn in acidic water (pH 5.1 – 5.9) was very low. An average of only 1 – 6 young were born per female, the result in comparison water (pH 6.0 – 6.8) being about 60 young. Thus a pH level of 5.5 – 6.0 is already critical for crayfish (Tuunainen et al. 1991).

Crayfish suffer in the same way as fish from the leakage of ions from the hemolymph (the "blood" of crayfish) via the gills into the water. Field observations showed that crayfish in fast-flowing, oxygen-rich water were better able to withstand acidity than those in lake water. The young age classes of crayfish are lacking from acidic lakes. Not enough studies have yet been carried out on the overall effect of acidification on crayfish stocks and crayfish fishing.

9 THE HISTORY OF ACIDIFICATION IN FINLAND

The condition of the main watercourses in Finland has been monitored since the beginning of the 1960's. Observations prior to this period are sporadic and, in most cases, unreliable owing to the analysis methods used. The water analysis data for some of the largest rivers collected by the Hydrography Office during the period 1913 – 1931 appear to be the most comprehensive of the old material available for comparisons.

The alkalinity and chemical oxygen consumption results from old materials in which the analytical methods have remained the same, in principle, were compared with more recent results (Alasaarela & Heinonen 1984). It is clear that, during the observation period, a lot of changes have taken place in the catchment areas of rivers that may have altered the chemical properties of the water. However, a clear decrease in alkalinity, which is at its greatest during the spring flood, has taken place in all the rivers.

The sediment which accumulates at the bottom of lakes is a natural archive that can be used in investigating the history of the lake and its catchment area. Sediment research has been used to identify both the date and cause of the pH changes. The most widely used method involves determining the frequency ratios of diatoms with different pH optima at various depths of the sediment. The age of the sediment layers is dated by using the lead isotope (^{210}Pb) analyses. According to the studies carried out on acidification sensitive and acidified small lakes in Finland, there are both naturally acidified waters and those that have become acidified during the past decades (Tolonen & Jaakkola 1983, Simola et al. 1985, Tolonen et al. 1986, Huttunen et al. 1990).

Naturally acidic lakes have also generally become more acidic in recent decades. The mean change in alkalinity in the group of 30 lakes studied by Huttunen et al. (1990) was –46 $\mu eq\ l^{-1}$. The development curves of pH and alkalinity are presented as examples in Fig. 15. The curves have been prepared using those species whose acidity optima and tolerance were investigated in ca. 90 lakes in Finland (Huttunen & Turkia 1990).

Small forest lakes seem to have become acidified only in southern Finland in recent years (Fig. 16). Naturally acidic lakes are more common in central and northern Finland.

Studies on the history of acidification have shown that there are also other causes of acidification that are independent of the atmospheric pollution load. However, it is difficult to explain the general increase in acidification that has been observed this

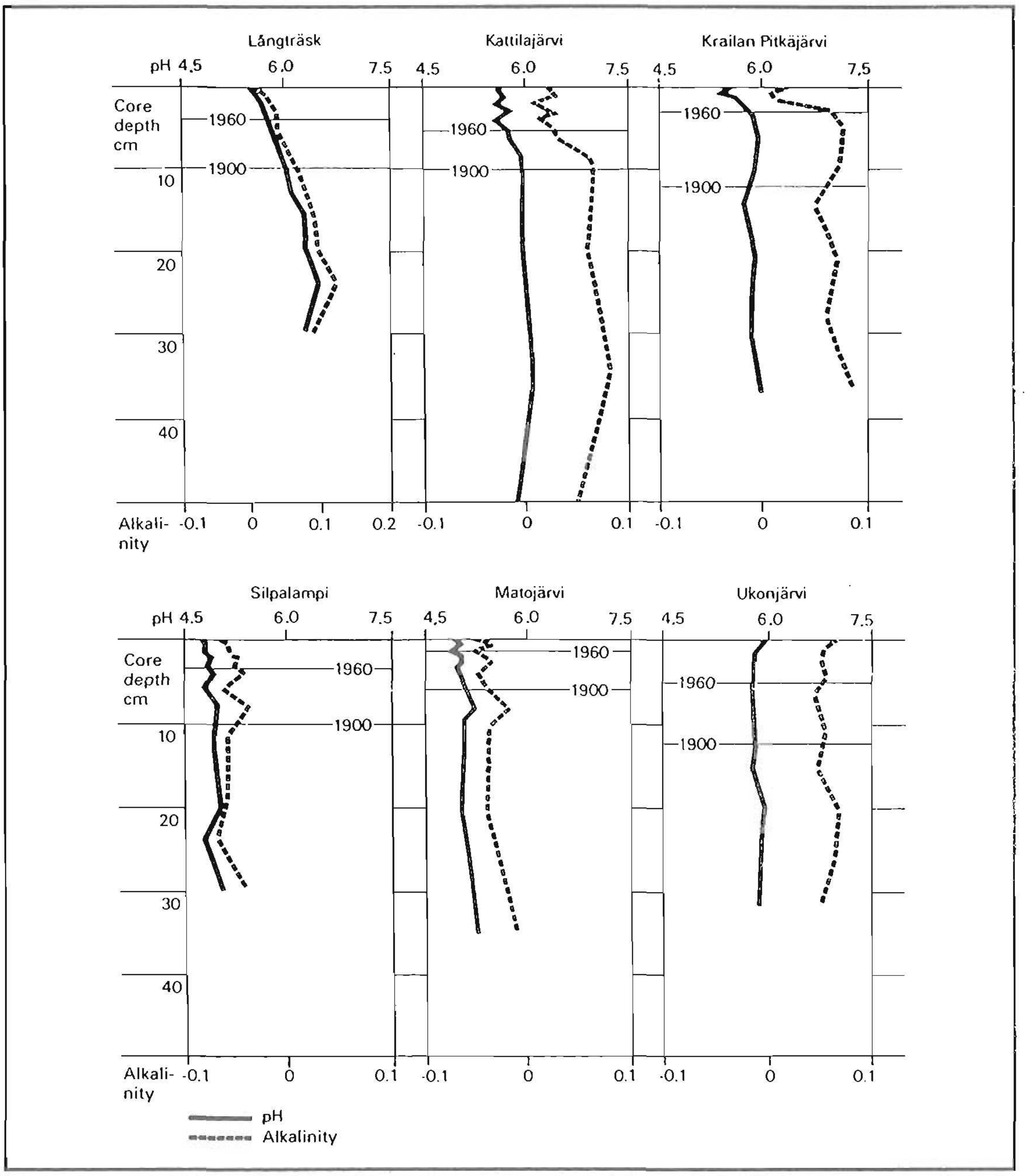

Fig. 15. Trend analysis of acidity and alkalinity based on diatom assemblages in lake sediment. The depth representing 1900 and 1960 is marked in the figure. Långträsk, Kattilajärvi and Krailan Pitkäjärvi have become acidified during the past few decades. Clear-water Silpalampi and brown-water Matojärvi are examples of naturally acifified lakes, and Ukonjärvi of a stable lake.

century by other means. The change in the ionic ratios caused by acidic precipitation and the matching of pollutants typical of deposition with bottom layers from corresponding periods, together with the diatom remnants indicating water acidification, may be sufficient evidence to show that acidic deposition has acidified a significant proportion of the small forest lakes in Finland.

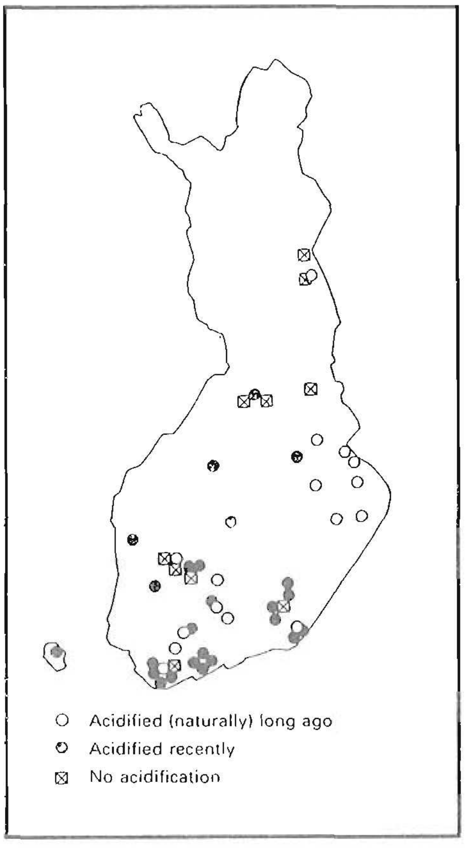

Fig. 16. Acidification–sensitive and acidic lakes studied using diatom analysis of the sediment.

10 LIMING OF ACIDIC LAKES

The losses of fish stocks in Finnish lakes have been small, compared with those in southern Scandinavia (Rask & Tuunainen 1990), and the liming of lakes is not a very common practice. Unlike the situation in Sweden, the liming of acidic lakes has not been subsidized by the state and the total number of limed lakes in Finland at present is not more than one hundred. Finnish governmental policy on air pollution is aimed at protecting ecosystems by reducing local and transboundary acidifying emissions, liming being regarded as a secondary means.

Liming as a mitigation method for acidic lakes was one topic in the Finnish acidification research programme. The technical part of the work compared the practical aspects of three spreading methods. Wet application in summer and dry spreading on the ice in winter were superior in effectiveness to dry spreading in summer. The ratios of the amounts of limestone powder required to achieve the same change in pH were 1 : 1.1 : 2.1 (wet : dry surface : dry). Dry spreading in winter was the most economic method in roadless areas (Alasaarela et al. 1990).

Brown organic substances, mostly weak acidic humic compounds, increased the specific neutralization requirement in acidic lakes (Fig. 17). The limestone powder requirement was over twice as great in typical brown water lakes with colour values

200 – 350 Pt mg l^{-1} as in corresponding clearwater lakes (Alasaarela et al., op. cit.). A small increase in colour values was measured after liming, amounting to between 7 % and 21 % at a target pH level of 6.5 in 5-day laboratory tests. The coagulation of humic substances after liming was relatively slight, only 1 – 16 % (measured as dissolved organic carbon, DOC) in the same test.

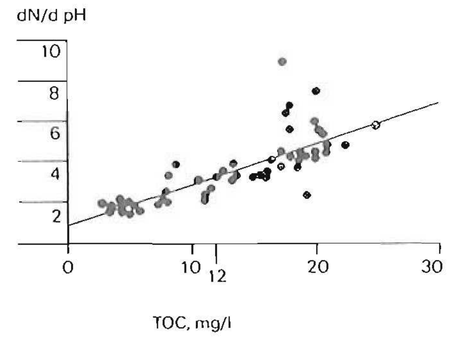

Fig. 17. Dependence of the specific neutralization requirement of water on the organic carbon concentration. Most of the organic matter comprises brown, dissolved humic substances. The mean organic carbon concentration in small lakes in Finland, 12 mg l^{-1}, is marked on the horizontal axis.

The limnological effects of liming were studied in several subprojects. The beneficial effects on fish were seen in the recruitment of new roach year classes in lakes with only sparse, old populations (Raitaniemi & Rask 1990).

The effects on macrophytes were slow. The *Sphagnum* population, which is typical of acidic clearwater lakes, vanished only some three years after liming, just before the chemical effects of the limestone disappeared (Helminen et al. 1989).

The primary productivity of acidic clearwater lakes increased markedly after liming due, at least in the case studied, to a 2.5-fold increase in inorganic nitrogen. The number of phytoplankton species increased and the species composition changed (Niinioja et al. 1990). In a polyhumic lake the most prominent change was a 50 % increase in bacterioplankton (Salonen et al. 1990). There was a decrease in the abundance of *Peridinae* and an increase in chlorophycean and chrysophycean species in clearwater lakes, while the relative biomass of dinophytes, chlorophytes and cryptophytes increased in a polyhumic lake (colour 170 Pt mg l^{-1}) and an acidophilic diatom, *Asterionella ralfsii*, decreased (Niinioja et al., op. cit., Salonen et al., op. cit).

In the zooplankton, the acid sensitive *Daphnia* populations increased after liming, but predator – prey relations in zooplankton and fish populations are very complicated and differed from one lake to another (Salonen et al., op. cit).

The number of macrozoobenthos species increased 2 to 3-fold within two years of liming. The recruitment of new sensitive species was rapid, but they rapidly disappeared as the lakes reacidified after liming (Helminen et al., op. cit.). Since most acidic lakes have originally been highly oligotrophic, liming may produce only slight eutrophication, even if the relative change is a marked one.

Reacidification is the biggest problem in the liming of lakes (Fig. 18). Lakes of short residence time should be limed using continuous dosing equipments or by liming hydrologically active parts of the drainage area such as wetlands or the banks of brooks. Another problem is what to do with naturally acidic humic lakes (Fig. 19), which underwent primary acidification thousands of years ago, even though their acidic status may have been accentuated by airborne anthropogenic acidification during the last 30–40 years.

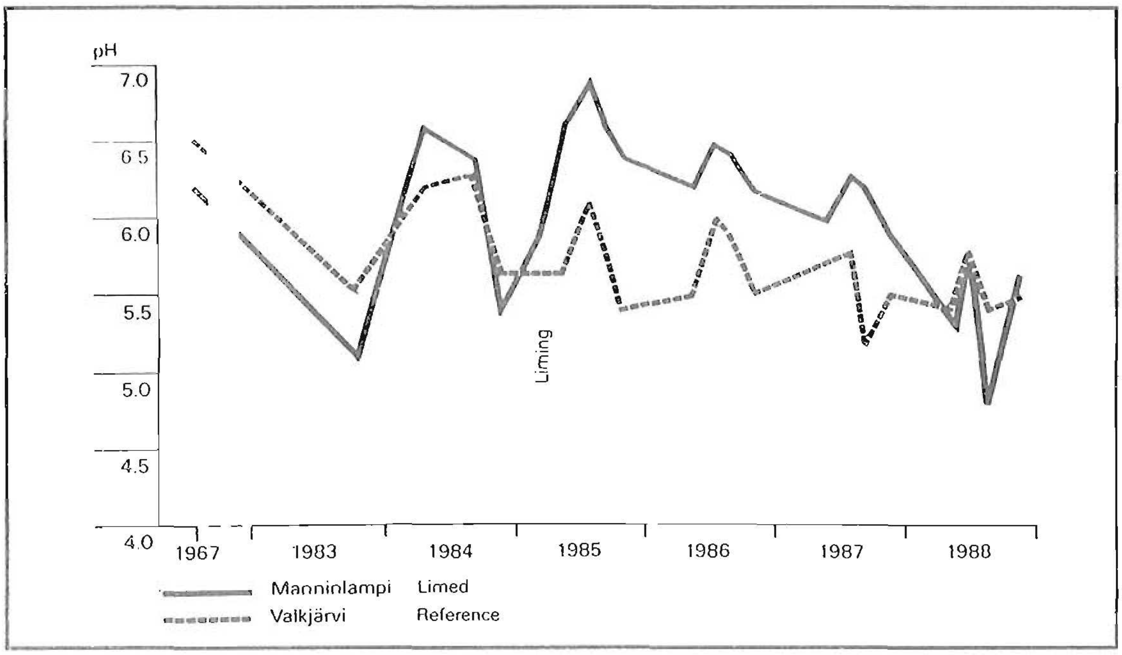

Fig. 18. Development of acidification in Manninlampi (limed) and Valkjärvi (reference lake). Manninlampi was limed in winter 1985. Both the annual variation in natural acidity in the lake and the weakening of the liming effect can be seen (Helminen et al. 1989).

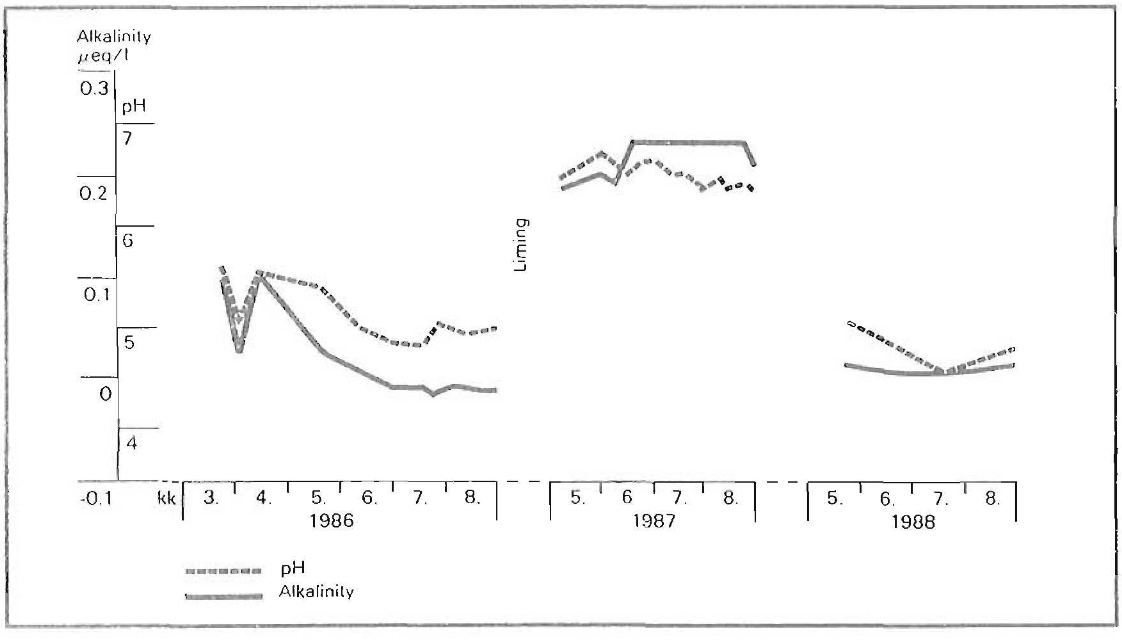

Fig. 19. Development of acidification in Pussijärvi, Evo. Limed in winter 1987. Liming had an effect only during the first year in this short retention humic lake.

11 APPLICATION OF MATHEMATICAL MODELS

The application of mathematical models was one of the key topics in the Finnish Acidification Research Programme. International co-operation was promoted especially with the International Institute of Applied System Analyses (IIASA), where Finnish researchers actively took part in developing the integrated RAINS model (Regional Acidification Information and Simulation) system. In 1988 the HAPRO project organized an international meeting on modelling, too (Kämäri et al. 1990b).

In modelling the long-term development of surface water acidification in Finland, the regional RAINS Lake Module (RLM) model was generally applied. In order to evaluate possible uncertainties when incorporating the RLM model, comparisons were made with the RLM model and the more complex MAGIC (Model of Acidification of Groundwater In Catchments) model using the data of small lakes with known historical diatom inferred pH development (Kämäri et al. 1990a). In order to obtain as comparable results as possible, the MAGIC model was run with calibrated input values from the RLM. The Monte Carlo parameter estimation procedure was used in both models to evaluate the uncertainty in the predictions of the models. The selected period of the acidification reconstructions was from 1850 - 1980.

Both models were found to satisfactorily outline the general time development of lake acidity. The increase in acidity was better described by MAGIC reconstructions, which also had higher "preacidification" values of pH and alkalinity. This is probably caused by the more detailed description of the buffer processes in catchment soil compared with the RLM (Kämäri et al. 1990a).

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ENTRANCE OF CHEMICAL SUBSTANCES WITH PRECIPITATION IN KARELIA

Lozovik P.A. and Basova S.V.
Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute

185003 Petrozavodsk
Urickogo 50
Russia, Republic of Karelia

1 INTRODUCTION

Acidification of the surface water is the most progressive form of anthropogenic influence on the environment (Izrael et al. 1983). The decrease in the pH of the water column increases the toxic effects of other pollutants and can be the cause of their transfer from bottom deposits and suspensions to the water column.

Consequently, current interest has been towards investigations directed to the study of the range and consequences of this phenomenon on the water ecosystems of various world regions, the assessment of the resistance of water bodies to acidification and the elaboration of the recommendations for the restoration of acidified basins.

Karelian surface waters are noted for their very low mineralization (25 mg l^{-1} on average) and low alkalinity levels, resulting in their small buffering capacity and weak resistance to acidification. Precipitation in Karelia, always acidic (pH 4.8) with considerable content of sulphates, nitrates and ammonium, is a potential danger as a source of acidification and contamination of surface waters.

Taking into consideration the importance of the water acidification problem for the Karelian hydrogeographical region, an investigation on this topic was carried out in 1989 – 1991 by the Water Research Department of the Karelian Research Center. Study of the chemical composition of precipitation was an integral part of this work. Some data of three Karelian regions – Lake Onega (Kondratyev et al. 1988), Vendyury region (Kharkevich 1986) and the iron-ore deposit of Kostamus (Feoktistov and Salo 1990) were obtained earlier. Data on the precipitation chemistry for the entire Karelian territory were practically absent. Such observations are not carried out by the Karelian Hydrometeorological Centre. Thus one of the tasks was to carry out the precipitation study for the entire territory of Karelia.

2 MATERIALS AND METHODS

Snow samples were selected in the central stations of the large Karelian lakes in 1988, and in the region of industrial centers (Segeza, Kondopoga, Nadvoitsy) in 1991 and rain samples in 1989 - 1990 in the 20 meteorological stations of the Karelian Hydrometeorological Centre (Fig. 1). In addition, the long-term precipitation study of the Vendyury region was continued as a part of the acidification programme.

Snow samples were taken throughout their depth with a plastic shovel in polyethylene sacs. In the laboratory, the samples were melted at room temperature, and snow water analyses were then performed.

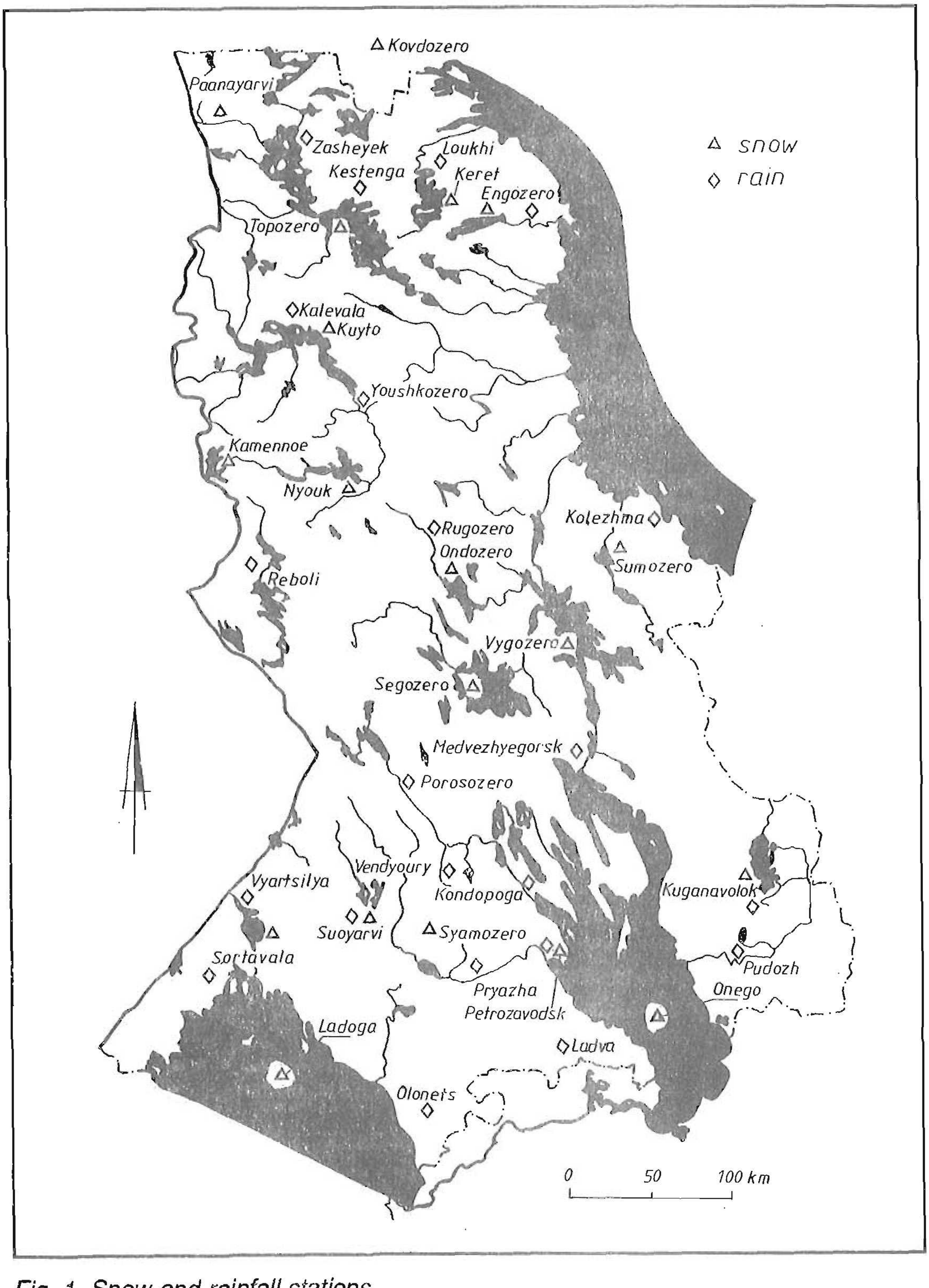

Fig. 1. Snow and rainfall stations.

Rain samples were collected in 1989 at the meteorological stations with the help of a polyethylene film one meter above the ground; in 1990, a special polyethylene sampler 50 cm in diameter was used. After the rain stopped, samples were poured into a polyethylene bottle. When at least two liters of water had been obtained, the samples were transported to the laboratory by mail. Samples of both fresh-fallen rain and rainfall collected during certain time periods were analysed.

Chemical analyses of the snow and rain water were carried out by the methods used in hydrochemistry for the surface water analysis (Table 1). It is necessary to note the sulphate analysis. There are no methods of direct sulphate determination. Classic methods are based on the sulphate binding with barium and on the determination of the latter in the solution or on the determination of the strong acid anion sum. In this study, sulphates were determined from the difference of the strong acid anion sum and the Cl^- and NO_3^- concentration (mg-eq l^{-1}). This method gives satisfactory results for the analysis of the low-chromatic waters. Matching of the cation sum with that of anions and the simultaneous obšervaton of the water electrical conductivity with that calculated according to the ionic composition may be a good test for the analysis accuracy. The presence of the fulvic-carbon acids in the analysed water leads to the exaggeration of the strong acid anion sum. To calculate the sulphate content it is necessary to subtract the concentration of the organic acid carboxylic groups.

Table 1. Analytical methods (Manual of Chemical Analysis of Surface Water 1977).

Parameter	Analytical method
pH	Potentiometric determination with glass electrode
Hardness	Trilonometric determination with chromogen
Ca^{+2}	Trilonometric determination with murexide
K^+, Na^+	Flame-photometric determination
Fe (total)	Colorimetric determination with o-phenantroline, λ = 510 nm
HCO_3^-	Titrimetric determination by Gran
Cl^-	Mercurimetric determination with diphenyl carbazone and bromiphenol blue
F^-	Ion-selective electrode
SiO_2	Colorimetric determination with ammonium molybdate in the form of yellow heteropoly acid, λ = 410 nm
NH_4^+	Microdiffusive method and ammonia colorimetric determination with Nessler reagent, λ =430 nm
NO_3^-	Reduction up to NO_2^- on Cd-column and NO_2^- determination
NO_2^-	Colorimetric determination with Griss-Illosvai reagent, λ = 536 nm
NH_4^+ + N org.	Organic reduction by Kjeldal and microdiffusive determination of ammonia
PO_4^{-3}	Colorimetric determination with ammonium molybdate and ascorbic acid, λ = 880 nm
P total	Oxidation with $K_2S_2O_8$ and determination of PO_4^{3-}
C organic	Photochemical determination in the system of continuous gas current
SO_4^{2-}	Difference from the sum of strong acids and Cl^- and NO_3^- contents

3 RESULTS AND DISCUSSION

3.1 Quality of rainwater

Precipitation over Karelia is always acidic with pH ranging from 4.1 to 6.6 (Table 2). As a rule, hydrocarbonates are absent and pH is less than 5.6, i.e. lower than the value corresponding to the CO_2 equilibrium concentration in precipitation. Precipitation contains an excess of the strong acidic anions (SO_4^{-2}, NO_3^-, Cl^-) in comparison with the main cations (Ca^{+2}, Mg^{+2}, Na^+, K^+), thus causing surface water acidification and a decrease in the water alkalinity. Snow water is usually more acidic than rain water. This is due to the fact that in summer there is more dust in the atmosphere resulting in partial acid neutralization through the interaction with carbonate and silicate suspended particles. NH_4^+, Ca^{+2}, Mg^{+2} predominate in the cation composition of snow water; NH_4^+, Ca^{+2}, Na^+ prevail in rain water.

The presence of NH_4^+ in the precipitation is attributed to the atmospheric gaseous ammonia and to the increase in its absorption by acidic aerosols. Ca^{+2} and Mg^{+2} predominate in terrigenous particles whereas Na^+ is supplied by the sea.

Anions in the precipitation are represented by sulphates, nitrates and chlorides. Sulphate content on average is 3.4 mg l^{-1}, chlorides 0.7 mg l^{-1} and nitrates 1.7 mg l^{-1}. Chlorides are of sea origin, sulphates and nitrates are mainly of anthropogenic origin due to the gaseous emissions in fuel combustion and raw material processing. Higher content of nitrates in snow water as compared to rain and the inverse result for chlorides is marked in the precipitation of Karelia. Sulphate content in these waters are nearly equal.

Background element content in the precipitation can be calculated according to the chloride ratio with other ions in the rain water and condensates above the ocean (Table 3).

Table 2. Chemical composition of precipitation in Karelia (mg l^{-1}), 1989 – 1990, n = 115.

	Ca	Mg	K	Na	HCO_3	SO_4	Cl	Σi	pH
Mean	0.51	0.28	0.23	0.37	0	3.36	0.72	6.1	4.8
SD	0.41	0.33	0.19	0.09	0	1.54	0.19	2.4	

	N-NH_4	N-NO_3	N-NO_2	P_{min}	P_{tot}	Si	Fe	Mn	Corg
Mean	0.38	0.40	0.02	0.012	0.024	0.19	0.03	0.02	1.20
SD	0.31	0.10	0.02	0.005	0.009	0.22	0.03	0.02	1.10

According to the comparison of background concentrations with observed values, it can be shown that Na^+ just as Cl^- is wholly of sea origin in the precipitation, Mg^{+2} by 30 – 40 %, K^+ by 20 – 50 %, Ca^{+2} by 10 – 15 % and SO_4^{-2} only by 5 – 8 %.

The organic carbon concentration in the rain and snow waters varies within the range of 0.04 to 4.8 mg l^{-1} (average value 1.2 mg l^{-1}), characterizing them as waters with very low content of organic matter. The organic carbon concentration is, in rain water, somewhat higher than in snow, causing rain water to be more coloured than snow water. Their chromaticity is, as a rule, less than 3 degrees. According to the permanganate and dichromate oxidability and BOD_5 and BOD_{20} values, organic matter in precipitation is rather stable to permanganate oxidation, and a considerable amount of its contituents are oxidized biochemically (Kharkevich 1986).

The essential difference of precipitation in comparison with surface water is the higher content of biogenic elements, nitrogen and phosphorus. According to the data of snow water analyses, nitrate nitrogen ($N-NO_3$) predominates over ammonium nitrogen ($N-NH_4$), and organic nitrogen (N_{org}) is less than $N-NH_4$. Amounts of ammonium and nitrate nitrogen are nearly equal in rain water, but organic nitrogen occurs less than mineral forms. In surface waters, the organic form usually prevails over the mineral form. Comparison of the nitrogen substance content in the precipitation and surface waters reveals that $N-NH_4$ and $N-NO_3$ in the former are 5 – 10 times higher than in the latter, and N_{tot} is, respectively, 2 times higher. Therefore, precipitation is an important source of nitrogen substances, in particular, mineral nitrogen forms for the water basins.

Total phosphorus (P_{tot}) content in precipitation is rather high. Its concentration reached 0.5 mg l^{-1} in the individual rain samples. In the snow water all phosphorus is represented in its mineral form but in the rain samples only by 50 %. The high organic (P_{org}) and total phosphorus concentrations observed are in some cases connected with the fact that terrestrial plants excrete volatile phosphine (Anon. 1977) which can be oxidized photochemically under the influence of a lightning arrester into phosphoric acid forming stable aerosols. This is apparently the reason for the high P_{tot} content in rain water.

The presence of silicic acid in the rain water can be an indication of mixed solid and liquid precipitations. In some rain samples its concentration reached 1.8 mg l^{-1}, with an average content of 0.2 mg l^{-1}. Iron (Fe) and manganese (Mn) content in precipitation is very low; their concentrations are at the level of 0.02 mg l^{-1}.

3.2 Regional variation

As the sample frequency in the whole Karelian territory was not sufficient to characterize every item, comparisons were only made in those regions where multiple observations were available.

Long-term observation on the precipitation composition has been carried out in the Vendyury Post. Rain waters of 1990 in the region of Sulazhgora Meteorological Station were investigated in more detail than elsewhere. Chemical monitoring of precipitation has been carried out since the beginning of the 1970's on Finland's territory, important data on the precipitation chemistry have been obtained. In Finland, calculations were performed in the following boundary regions: Kurvinen, Kuhmo, Valtimo, Naarva, Kuusjärvi, Punkaharju and Kotaniemi (Järvinen and Vänni 1990a, b).

The chemical composition of precipitation in the Vendyury region differs slightly from that of Karelia as a whole. The difference consists in the lower content of the mineral forms of nitrogen and higher organic nitrogen share in the Vendyury precipitation as compared with the data on Karelia as a whole. There are no significant differences in the chemical composition of rain water in the Vendyury region under various wind directions. Therefore, it is possible to conclude that in Karelia the composition of precipitation depends only slightly on meteorological conditions. It is close to that of the adjacent territories that is apparently stipulated by the character of atmospheric phenomena: alteration of the cyclone and anticyclone processes.

Differences between snow and rain waters observed in Karelia are characteristic of Finland, too. Higher nitrate content and lower pH values in the snow water as compared with rain water were revealed. Precipitation in Finland is more acidic than in Karelia. It contains less Mg^{+2} which can be connected with methodical inaccuracy. In other respects precipitation chemistry in Finland is very close to that of Karelia.

The effect of large industrial centers on the chemical composition of precipitation was also studied. Close disposition of a silica brick plant led to the increase in Ca^{+2} and silicic acid concentration in the rain water of the Sulazhgora region, and the nearby location of the Petrozavodsk Heat Central Station led to the considerable nitrate nitrogen (1.4 mg l^{-1} N) and even nitrite nitrogen content (up to 0.05 mg l^{-1} N) that was not observed in any other precipitation sample.

Snow samples collected in Segeza, Kondopoga and Nadvoitsy regions were acidic (pH ranged from 4.8 to 5.9). Changes in the biogenic elements and Cl^-, Na^+, K^+ contents at greater distances from the town were not observed.

Higher Ca^{+2}, Mg^{+2}, Si, SO_4^{-2}, F^- contents were observed in the 5 km zones near the industrial centers. The average SO_4^{-2} and F^- concetrations are shown in Fig. 2. It can be concluded on this basis that there is a local increase in some ions concentrated in precipitation near the contamination centers. Thus the effect of Nadvoitsy Aluminium Works results in the F^- content increase in precipitation (with an average F^- concentration of 1.9 mg l^{-1} in the 0 - 5 km zone), and that of the Segeza Papermaking Plant, in the sulphate content increase in the snow collected within the 5 km zone (12 mg l^{-1} on average).

Increase in the F^- concentration in precipitation collected 15 km from Segeza and that of SO_4^{-2} 15 km from Nadvoitsy can be explained by the combined effect of Segeza and Nadvoitsy. The content of all components in the region of Kondopoga's industrial center is less than that in the regions of Segeza and Nadvoitsy. The characteristic impact contamination zone was not observed at Kondopoga.

Data obtained from the precipitation chemistry was used to assess total amounts of chemical elements falling out with liquid precipitation on the territory of Karelia (Table 3). An average annual sum of precipitation in Karelia, equal to 575 mm per year (Atlas of Karelian ASSR 1989), was taken for calculation.

Sulphates compose the main part of the ions in precipitation (63 % of the total salt and acid amount). Their anthropogenic origin is valued as 1.8 t km^{-2} a^{-1} (94 %) for Karelia, 1.6 t km^{-2} a^{-1} for Finland and 1.8 t km^{-2} a^{-1} for Kola Peninsula. The data for Karelia, Finland and Kola Peninsula are very similar. Significant differences in Mg^{+2} values are connected with use of various analytical techniques. In some extent it is also seen with Cl^-.

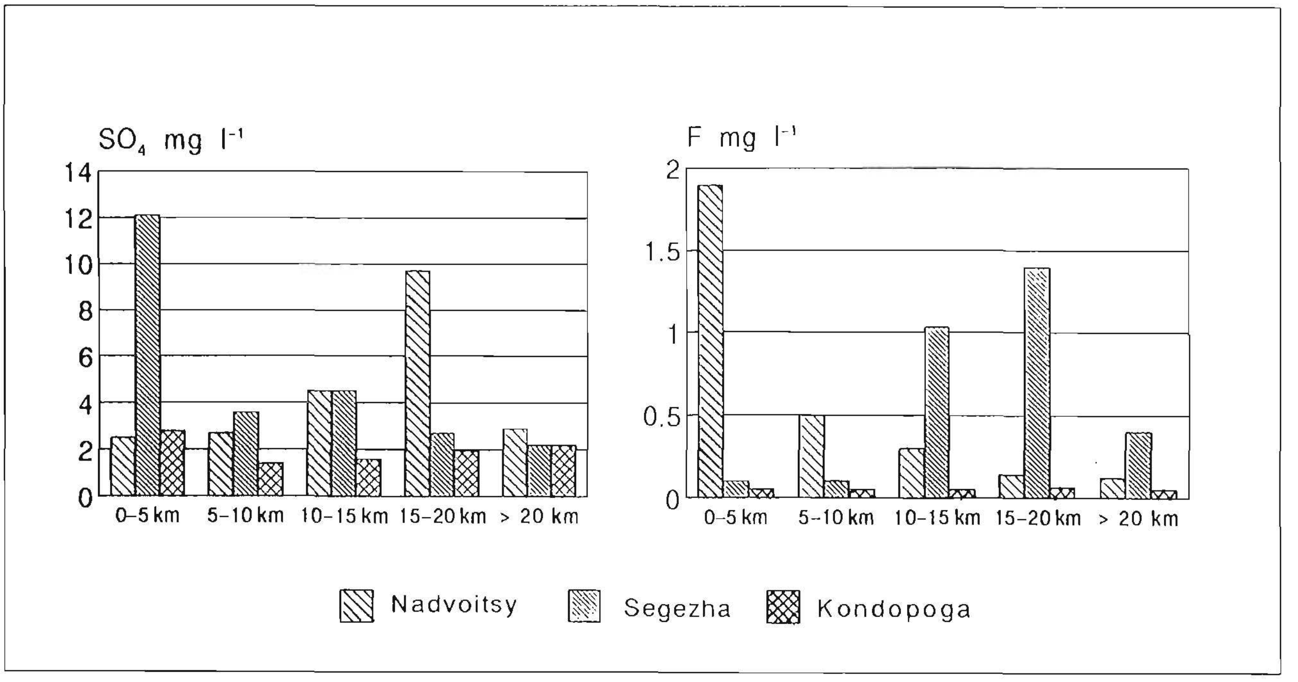

Fig. 2. The sulphate and fluoride concentrations in snowmelt water in different regions.

Table 3. Fallouts of chemical elements on Karelia territory (mg m^{-2} per year)

	Ca	Mg	Na	K	SO_4	Cl	Σi	Sum of strong acids (mmol m^{-2} a^{-1})
Total	290	160	210	90	1930	360	3040	11
Background	30	40	210	30	100	360	790	0
Anthropogenic and non-sea	260	120	0	60	1830	0	2250	11

Strong acid fallout in Finland is 1.5 times higher than in Karelia. The reason may lie in the fact that Finland is influenced to a greater extent by the transboundary transport from Western Europe as compared to Karelia. Therefore, the process of water acidification may have more negative effects in Finland than in Karelia.

The fallout of biogenic elements on Karelian territory is as follows:

$N-NH_4$	$N-NO_3$ mg m^{-2} a^{-1}	P_{tot}
250	230	14

The fallouts of total nitrogen (N_{tot}) and total phosphorus (P_{tot}) are nearly 700 kg and 1.4 t km^{-2} a^{-1}, respectively. In Finland fallout of the mineral forms of nitrogen is slightly higher, and that of organic nitrogen is less than in Karelia.

4 CONCLUSIONS

The precipitation of Karelia is acidic, with pH ranging from 4.1 to 6.5. The content of strong acids (H_2SO_4, HNO_3) in precipitation is on average 0.016 mmol l^{-1} which may cause some change in the alkalinity and pH of water basins depending on the basin's hydrological state and geomorphology. Anthropogenic sulphur content in the precipitation is 92 – 97 %. The total fallout of sulphate is 1.8 t km^{-2} per year, that of strong acid is 11 mmol m^{-2}.

Precipitation in Karelia is one of the important sources of biogenic element (ammonium, nitrates, phosphorus) input to surface waters.

According to its chemical composition and amount, the precipitation of Karelia resembles that of Finland.

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SNOW CONTAMINATION CAUSED BY AN ORE-DRESSING MILL

Feoktistov, V.M.
Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute
185003 Petrozavodsk
Urickogo 50
Russia

Lazareva, I.P.
Karelian Research Center
Russian Academy of Sciences
Forest Research Institute
185610 Petrozavodsk
Pushkinskaya Street 11
Russia

1 ABSTRACT

A number of chemical indices (pH, SO_4, Cl, HCO_3, Ca, Mg, K, Na etc.) in snow water in the vicinity of an ore-dressing mill have been studied. The results obtained have shown that the impact zone is restricted to 6 – 8 km from the source of discharge and is indicated by a rise in the pH of snow water against regional snow acidification. The resultant arrays of chemical parameters for meltwater have been processed using both factor and discriminant analyses.

2 INTRODUCTION

Snow cover is known to be a natural accumulator of substances transported by wet and dry precipitation from the atmosphere. It is possible to reveal major contaminants and to determine both the structure of their precipitation and the distance of transport during the cold season by studying the chemical composition of snow water (Vasilenko et al. 1985).

Industrial pollution is especially harmful for the nature of northern areas. The study of precipitation in the vicinity of the Kostomuksha ore-dressing mill in northern Karelia is, therefore, of great interest. It should be noted that the ore-dressing mill is the only big industrial enterprise in northern Karelia. It discharges annually about 60 000 tons of pollutants to the atmosphere of which over 90 % is sulphur dioxide.

Our purpose was to study the the precipitation density, qualitative composition and environmental distribution of pollutants.

3 MATERIAL AND METHODS

In 1987 – 1990, the snow samples taken near the mill were studied hydrochemically as part of ecological monitoring (Fig. 1). The sampling sites were spaced 2 km apart within 0 – 6 km, 5 km apart within 6 – 15 km and 25 km apart within 15 – 60 km from the source of discharge. Samples were taken between the last ten days of March and the first ten days of April, a period of maximum moisture reserve in the snow. A plastic tube was used to sample the entire snow column. Sampling sites were chosen in the open landscape (a lake or a bog). Additional samples were taken in large forest "windows" in 1987. Field and analytical studies were conducted using the recommendations described in Anon. (1977) and Anon. (1981).

The pH, electrical conductivity and hydrocarbonates of the water were determined in the laboratory after complete snow melting. The whole sample was then run through a membrane filter (0.45 μm) and the filtrate was analysed by coventional methods. Concentrations of Fe, Mn, Zn, Ni, Co and Cu were determined by the atomic absorption method with preliminary 20–fold concentration. The weight of the solid precipitate settled on the filter was analysed by the X–ray fluorescence method.

In the observation area, the snow cover was formed in November and stayed till mid–April. As a result of a warm spell in late March in 1988, the snow subsided (its height was 38 cm), packed and saturated with water from the lower layers (Fig. 2).

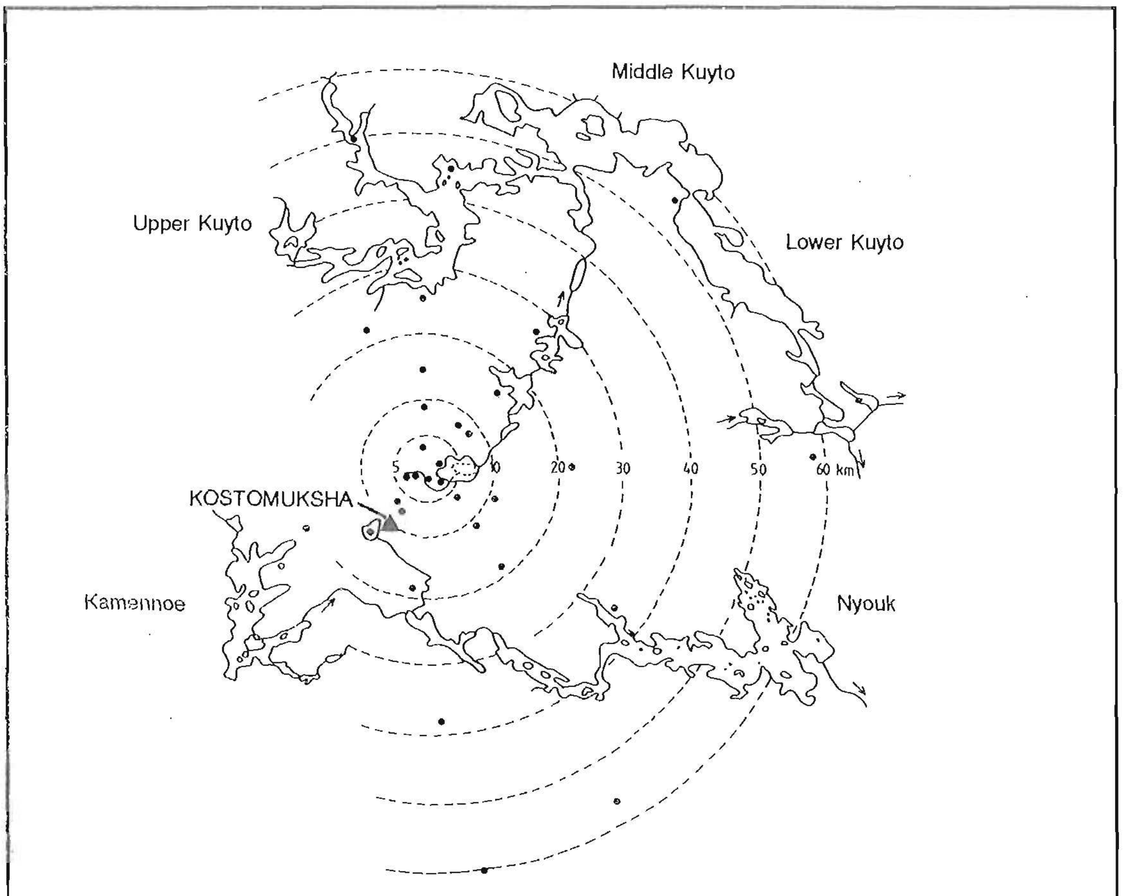


Fig. 1. The research area.

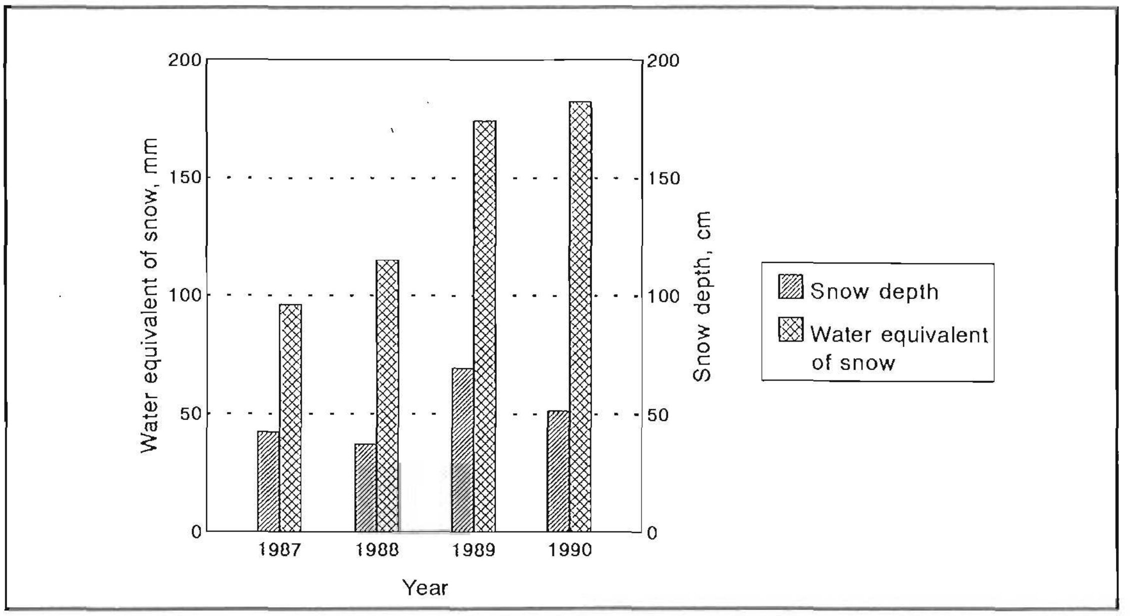


Fig. 2. The height and water equivalent of snow cover in 1987–1990.

4 RESULTS AND DISCUSSION

4.1 Variation in the chemical composition of snow in studied areas

Chemical analyses of snow water obtained over four years have shown that the concentrations of individual components are quite comparable (Table 1).

In the study area, the snowmelt water is acidic. At all sampling sites, except for the nearest ones (6 – 8 km away), the pH of water varied from 4.6 to 4.9, which corresponds to average values for Finland (Kauppi & al. 1990, Soveri 1985). The pH of water increased toward the mill to reach pH 5.7 – 6.1 (Fig. 3). This is due to the fallout of dust which contains both alkali and earth metals. The pH value is affected by weather. Thus, a few warm spells recorded in the spring of 1988 caused pH values to increase by 0.3 – 0.4 units. According to Kubin and Lippo (1987), the beginning of snow melting substantially charges the distribution pattern of the chemical indices of snow water.

The distribution of weighed substances (dust) in the snow water, in the vicinity of the mill, was not uniform. Coarse dust fell down near the mill, whereas the finest particles were scattered over a large area. The above distribution provided a basis for recognition of the three following zones (Fig. 4):

- **zone 1** ; 0 – 6 km from the mill, with maximum dust fallout (dust content 21 – 81 mg l^{-1}),
- **zone 2** ; 7 – 25 km from the mill, with lower dust fallout (dust content 6 – 16 mg l^{-1}),
- **zone 3** ; over 25 km from the mill, with minimum dust content (3 – 7 mg l^{-1}).

Table 1. Average weighed concentrations of components in snow meltwater (mg l^{-1})

Parameter	Year	Year mean	Zones 0–6 km	7–25 km	over 25 km
pH	1987	4.9	5.8	4.7	4.6
	1988	5.2	6.1	4.9	5.1
	1989	5.0	5.7	4.8	4.7
	1990	5.3	6.2	5.1	4.8
Dust	1987	29.1±4.1	81.4±16.2	15.9±2,2	6.9±0.7
	1988	32,3±11.7	67.7±22.7	11.6±2.2	2.4±0.8
	1989	9.9±2.0	21.2±6.1	6.5±1.1	2.9±0.5
	1990	13.5±2.0	47.4	7.5±2.4	2.1
SO_4^{2-}	1987	2.4±0.2	2.5±0.5	2.6±0.1	2.0±0.3
	1988	1.7±0.1	2.0±0.2	1.9±0.1	0,9±0.05
	1989	1.7±0.1	2.0±0.2	1,7±0.1	1.5±0.2
	1990	0.8±0.1	1.3	0.7±0.1	0.8
Cl^-	1987	0.6±0.03	0.7±0.03	0.7±0.04	0.5±0.01
	1988	0.8±0.04	0.7±0.03	0.8±0.08	0.7±0.02
	1989	1.0±0.04	1.0±0.1	1.0±0.05	1.1±1.1
	1990	1.4±0.07	1.9	1.3±0.08	0.9
HCO_3^-	1987	1.0±0.1	2.7±0.3	0.5±0.1	0.4±1.1
	1989	2.3±0.5	5.5±1.4	1.2±0.3	0.6±0.3
	1990	1.7±0.8	8.4	1.4±0.1	0.0
Ca^{2+}	1987	0.7±0.08	1.3±0.1	0.6±0.08	0.2±0.03
	1988	0.8±0.1	1.9±0.4	0.5±0.05	0.3±0.01
	1989	0.6±0.1	1.4±0.3	0.4±0.04	0.2±0.03
	1990	0.8±0.2	2.1	0.5±0.05	0.3
Mg^{2+}	1987	0.2±0.04	0.3±0.02	0.2±0.05	0.05±0.01
	1988	0.2±0.03	0.5±0.02	0.2±0.01	0.1±0.01
	1989	0.2±0.01	0.3±0.03	0.3±0.02	0.2±0.02
	1990	0.2±0.03	0.4	0.3±0.03	0.2
K^+	1987	0.1±0.01	0.2±0.01	0.1±0.01	0.09±0.01
	1988	0.3±0.02	0.5±0.02	0.3±0.03	0.2±0.03
	1989	0.2±0.02	0.3±0.01	0.2±0.01	0.2±0.03
	1990	0.4±0.03	0.4	0.3±0.03	0.2
Na^+	1987	0.06±0.01	0.09±0.01	0.05±0.01	0.07±0.01
	1988	0.3±0.03	0.2±0.03	0.3±0.05	0.2±0.03
	1989	0.3±0.02	0.2±0.01	0.3±0.03	0.2±0.03
	1990	0.4±0.03	0.5	0.4±0.03	0,4
Fe_T	1987	93.4±18.8	82.9±7.2	75.2±5.7	55.7±6.0
	1988	57.0±5.1	70.0±10.4	61.0±7.5	34.0±4.0
μg l^{-1}	1989	77.3±12.7	91.0±22.5	74.1±14.9	65.0±15.5
	1990	111.9±11.9	121.5	121.4±15.8	36.0
Mn	1987	9.3±0.7	15.0±1.0	8.2±0.6	6.2±0.5
μg l^{-1}	1988	8.7±1.7	17.2±6.1	7.7±1.2	2.6±0.4
	1989	5.8±1.8	11.0±5.1	4.3±1.8	2.4±0.4
Zn	1987	18.5±1.1	22.4±1.2	17.7±1.1	16.3±0.8
μg l^{-1}	1988	29.2±2.3	28.1±4.9	31.7±3.6	24.6±3.2
	1989	21.1±1.2	23.0±2.9	26.0±1.5	17.0±1.7
	1990	27.3±1.9	28.2	26.7±2.1	20.6
Ni	1987	5.9±0.3	7.0±0.2	6.1±0.4	4.7±0.1
μg l^{-1}	1988	5.8±0.3	6.8±1.0	5.5±0.5	5.2±0.7
Cu	1988	2.8±0.2	2.6±0.4	3.0±0.3	2.7±0.7
μg l^{-1}	1990	2.8±0.2	3.4	2.7±0.03	0.9
Co	1988	8.6±0.6	6.5±1.5	8.1±0.8	11.9±0.8
μg l^{-1}					

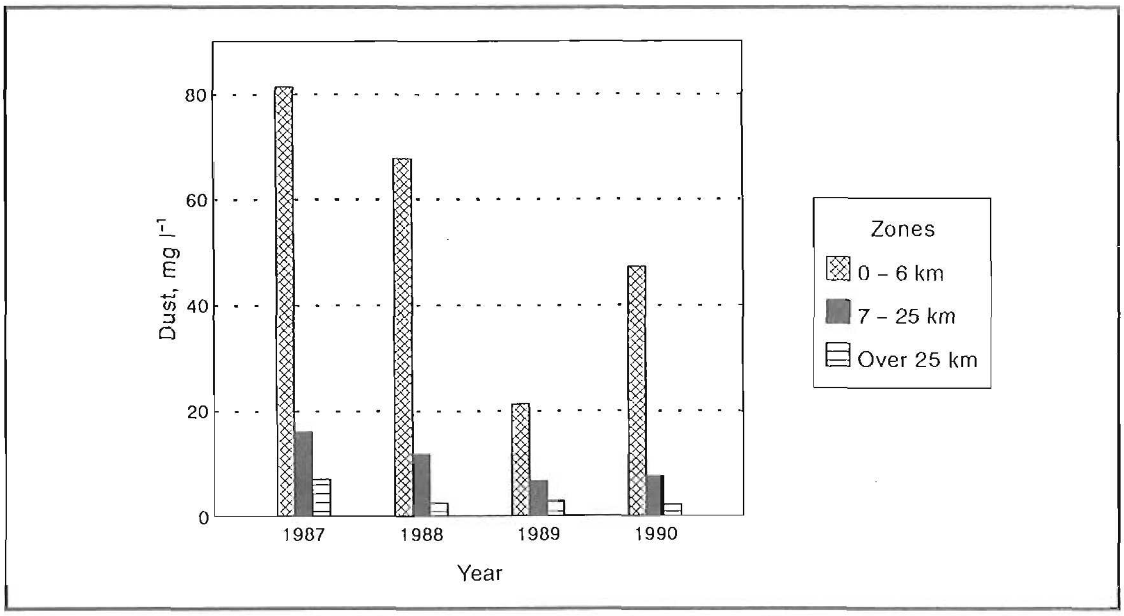


Fig. 3. The pH of water in the study area in 1987 – 1990.

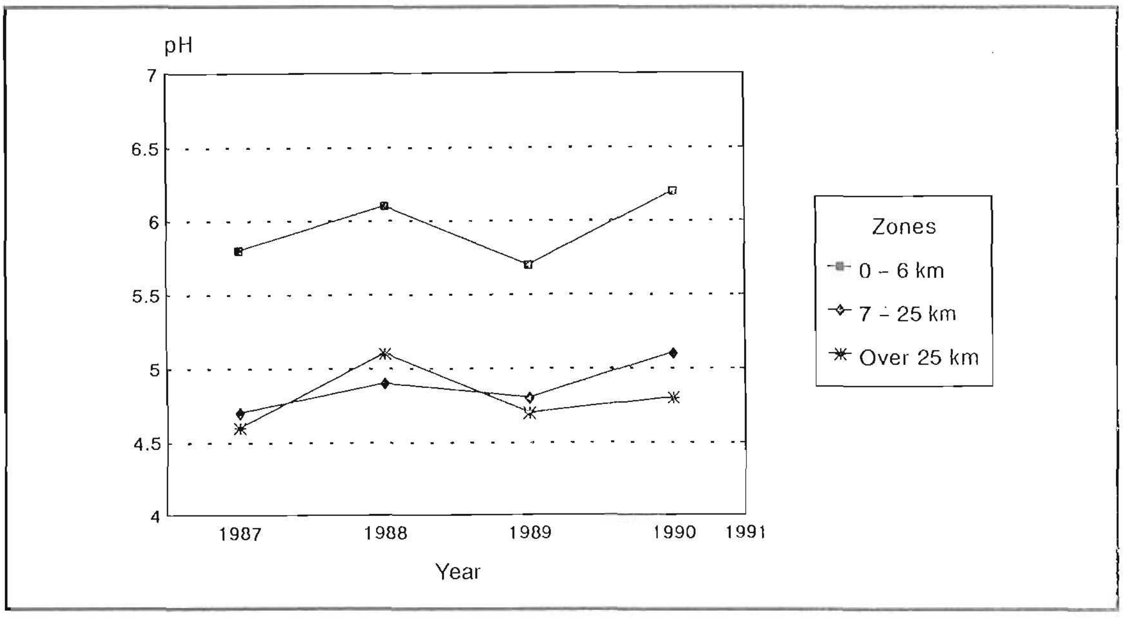


Fig. 4. The dust concentration in snow melt water in 1987 – 1990.

The anion composition of the water is dominated by sulphates, but their concentration is relatively low (0.9 – 2.5 mg l^{-1}, maximum value 6 mg l^{-1}). The above values are slightly higher than those for transboundary transport (Nazarov & al. 1984) and are close to the average sulphate concentration in the atmospheric precipitates of southern Karelia (Kharkevich 1986). It can be assumed that the bulk of sulphur dioxide is involved in distant transport before it is oxidised to sulphates, thereby increasing their concentrations in the snow. The weighted average concentrations of hydrocarbonate ions is 1.0 – 2.3 mg l^{-1}. The absence of the above ions in snow water is characteristic of some parts of Karelia unaffected industrially (Kharkevich 1986), therefore an anthropogenic origin can be assumed. The chloride concentration varied from 0.5 to 1.0 mg l^{-1}.

The cation composition is dominated by calcium ion. The total of calcium and magnesium ions is greater than the total of alkali metals. The macrocomponents of snow water form the following sequences on the basis of decreasing concentrations: SO_4 > HCO_3 > Cl and Ca > Mg > K > Na.

The meltwater of the study area is relatively poor in heavy metals (2 – 30 $\mu g\ l^{-1}$) and rich in iron (30 – 120 $\mu g\ dm^{-3}$), a major pollutant in mining industry. The following sequence was obtained on the basis of decreasing dissolved metal concentrations: Fe >> Zn > Co > Ni > Cu.

The chemical composition of dust in snow meltwater was analysed in 1987. As was expected, iron was most abundant among the elements revealed. The average iron concentration was 244 mg g^{-1}, the total of 17 elements being 270 mg g^{-1}. The sequence of indices studied can be divided into three groups:

a) **macroelements** (the content of each is more than 1 mg g^{-1}) such as Fe, K, Ca, Ti;

b) **microelements-1** (the content of each is less than 1 mg g^{-1} but more than 0.1 mg g^{-1}) such as Mn, Cr, Pb, Zn, Cu, Ni, Sr;

c) **microelements-2** (the content of each is less than 0.1 mg g^{-1}) such as Zr, Rb, As, Br, Mo, and Se.

Considerable spatial variation in both the amount of dust and the majority of chemical indices of snow water has been revealed in the area affected by atmospheric fallout.

4.2 Estimation of the chemical composition of snow by factor and discriminant analyses

The spatial variation in the results of chemical analyses has been estimated by using methods for multivariate statistical analysis (Lasareva et al. 1993).

The results of chemical analyses of snow meltwater made in 1987 – 1988 were used as input data. Correlation matrices were constructed on 14 – 22 variables depending on the number of components to be analysed for an individual year. The input data were represented as the concentrations of constituents (mg l^{-1}) and the fallout density of the substances studied (g m^{-2}). A matrix for the solid-phase (dust) composition of snow water was analysed for 1987.

The data obtained were processed on a ES-10-52 computer using BMDP 4M programme for factor analysis and a BMDP 7M programme for discriminant analysis (Anon. 1983).

The results of the factor analysis of the database for the fallout density of individual components obtained during the two years of study are given as an example (Fig. 5 a and b). Three factors that account for 73 % variance were recognized by analysing the data on the ionic composition of snow water obtained in 1987 and five factors (70 % variance) are based on the data for 1988.

The following interpretation of factors could be proposed for the 1987 database:

I. Factor I is represented by high loads for all analysed variables. It seems to generally characterize the pollution caused by the mill which is apparent as the fallout of coarse dust.

II. Factor II has high positive loads for Fe and the heavy metal total, as well as low negative loads for earth metals and the total amount of dust. It can be interpreted as the aerosol transport of heavy metals.

III. Factor III estimates the fallout density of sulphates.

The structure of the factors for the 1988 snow water data is largely the same as that of the previous year. However, two more factors, IV and V, that seem to be due to climatic conditions (a warm spell in early April), are low recognized.

Thus, assumptions on the nature of transported substances, based on the interpretation of each factor, provided a basis for distinguishing dust, aerosol and gas constituents in a general flow of substances.

Four factors responsible for 72 % variance were revealed by factor analysis of data on the fallout density for the components that make up the solid phase (dust) of snow water.

The correlation matrix of the above data indicates that the amount of almost all elements is closely related to total dust fallout density and that the elements are highly correlatable ($r = 0.6 - 0.9$). The first two factors are most significant in terms of factor variance values (Fig. 5 c). In factor I high loads are shown by Ti, Ca, Rb, K, Zn, Fe, and Zr, whereas in factor II by Sr and a group of heavy metals (Fe, K, Ni, Zn, Mn and Cu).

The element composition and some distributive charasteristics of factors, based on the gradient of pollution around the mill, led us to conclude that factor I can be used to characterize the litophile components of dust, and factor II to describe the transport of aerophilic heavy metals of industrial genesis.

Integral evaluation of aerogenic pollutants transported to the study area is of interest for those who investigate the consequences of aerogenic environmental pollution. Such information can be obtained by discrimant analysis.

Discrimant analyses was applied to the database on the chemistry of snow meltwater and its solid phase for 1987. The database was classified into nine groups: three zones and three directions in each zone. Whether a particular sampling site belonged to a certain group it was determined with a certain apriori probability by calculating it as a function of distance between the sampling sites and the center of each group. The probability that samples belonged to zone 1, at all sampling sites, was 100 %, to zone 2, 100 % in the center of the zone and 60 - 70 % at its boundary, and to zone 3, 60 - 70 %. The boundary of transition to zone 3, arbitrarily defined as pure, is within 21 - 27 km.

A

FACTOR	I	II	III
+1	ΣTM Ca+Mg		
	Ni K+Na D Fe Cl Mn Zn HCO_3 SO_4	Fe ΣTM	SO_4
		Zn	
LOAD		Cl	Cl Ni Ca+Mg
0		SO_4 Ni	Mn D
		K+Na	Fe ΣTM K+Na
		Mn HCO_3 Ca+Mg	Zn HCO_3
− 0.6		D	
δ^2	49.3 %	14.2 %	9.6 %

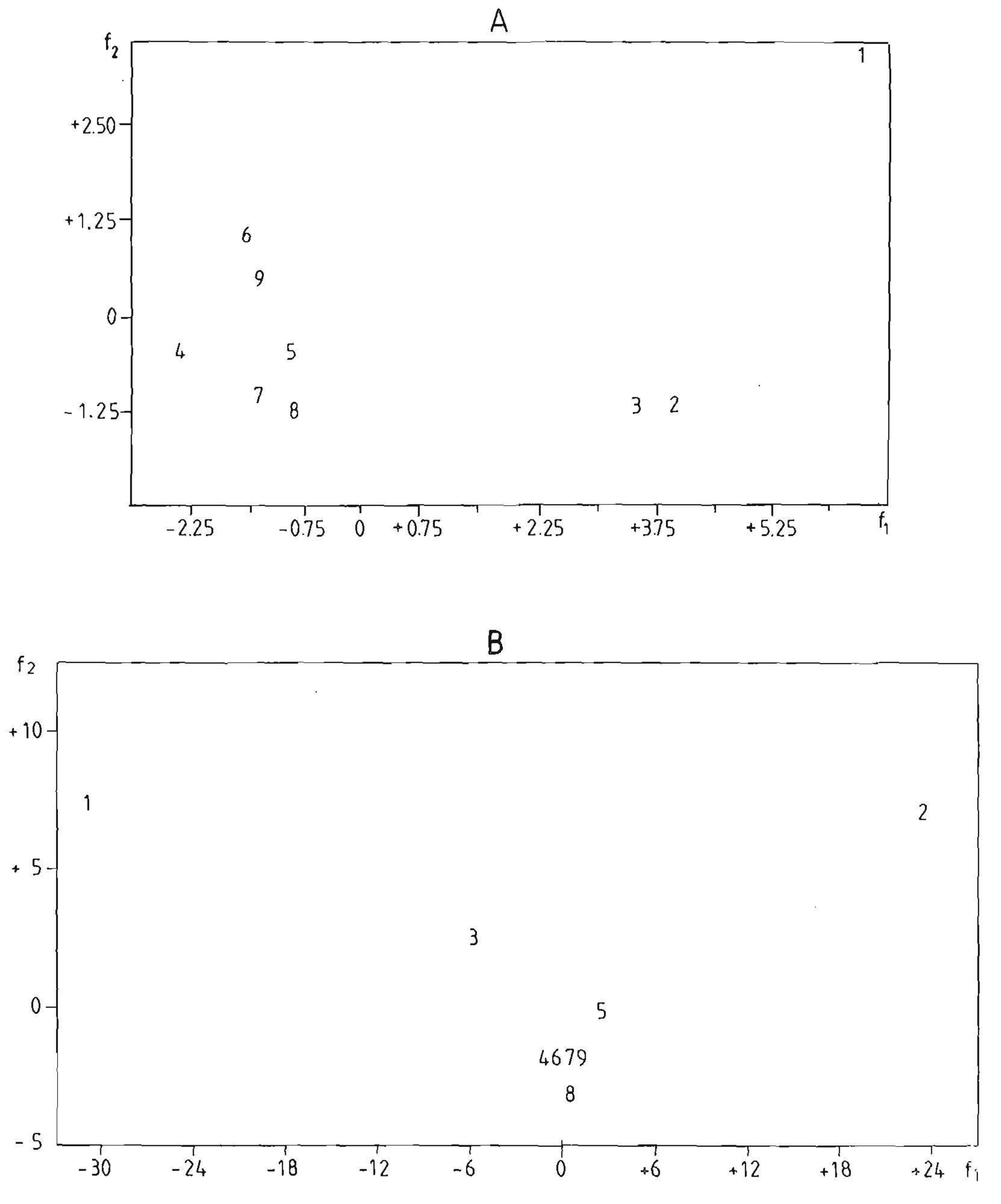
B

FACTOR	I	II	III	IV	V
+1	D Mn Ca+Mg		Co Ni		
	K+Na	Zn ΣTM Fe		Cl We	SO_4 Fe
	ΣTM	K+Na P		N SO_4	ΣTM We
LOAD	N Ni Fe	Cu Ni We Mn	Cu ΣTM We Ca+Mg	Cu P K+Na	Ca+Mg P Ni N
0	Zn SO_4 We	D Co Cl SO_4 N	Zn Fe Mn K Na P	Mg+ Zn Mn Ca	Mn Cu D
	Cu Cl P Co	Ca+Mg	SO_4 N D Cl	Ni D ΣTM Fe Co	Cl K+Zn Ca+ Na
− 0.6					
δ^2	29.4 %	13.1 %	13.5 %	7.3 %	6.3 %

C

FACTOR	I	II	III	IV
+1	D Ti Ca Rb	Sr		Sr
	K Zn Fe Zr	Fe K Ni	Cr Zn Mn	
	Br Cr Sr	Zn Mn Cu Ti Ca Zr	Fe Ni D Pb Ca	We Mn D
LOAD	Cu Se Ni Mo Mn	Rb Pb Se D	Se Zn Ti Sr Rb	Ni Br Rb Zn Cu Sr
0	We Pb	Cr We Mo Br	Mo K Cu	Ti Ca Pb Mo Cr
			Br We	Zn Fe K
− 0.6				
δ^2	28 %	34 %	5 %	5 %

Fig. 5. Factorial load of massives: A = deposition density (mg l^{-1}) of meltwater components in 1987; B = deposition density of meltwater components in 1988; C = dust deposition density (g m^{-2}) in 1987. D = dust, We = water equivalent of snow, TM = heavy metals.



Vector / Zone	Number of group		
	North	NE	SW
I	1	2	3
II	4	5	6
III	7	8	9

Fig. 6. Results of discriminant analysis. A = concentration of components in snowmelt water (mg l^{-1}) 1987; B = deposition density of dust (g m^{-2}) 1987; 1 – 9 = centers of the groups.

Furthermore, discriminant analysis helps to reveal the most significant variables in an array of input data. Among the components of ion composition pH and Na had the strongest effect on the spatial heterogeneity of sampling. The graphical representation of analytical results has shown that the sampling sites of zone 1 are clearly separated from others (Fig. 6 a), whereas those of zone 2 and 3 are not markedly separated.

K, Zn, Br, Zr, and Fe are the most significant variables for the solid-phase components of snow water. The existence of pollution zones is corroborated and the probability of sampling sites belonging to a certain zone is normally 80 –100 %. Zone 1 is clearly separated on the basis of the internal structure of sampling and the scatter of estimates for individual groups along the trends within this zone, is fairly large. All other groups (zones 2 and 3) are more uniform and form a single array with similar estimates (Fig. 6 b). Discriminant analysis can be used to determine whether it is correct to divide database into groups corresponding to pollution zones and direction from the source without analysing in detail the behaviour of each element.

5 CONCLUSIONS

It has been shown in this study that the source of pollution is clearly indicated by all hydrochemical indices, the most convincing one being a rise in the pH of snow water against regional snow acidification. The distribution of meltwater sulphates over the territory surrounding a source of pollution suggests that the bulk of sulphur dioxide is involved in remote transport.

Factor analysis was used to reveal some factors (processes) that substantially affect the chemical composition of water, namely the dust (coarse fraction), aerosol and gas transport of pollutants. The first one affects the ion composition of meltwater and predominates in the vicinity of the mill. The second and the third factors are related to the distribution of heavy metals and sulphur oxides (sulphates) and are observed in the course of sampling.

Discriminant analysis has confirmed that the atmospheric precipitates detected in the impact zone greatly differ in their properties. Furthermore, discriminant analysis has been used to reveal the following indices to be most significant for the zoning the territory: pH and Na for ion composition and K, Zn, Br, Zr and Fe for the solid phase of snow meltwater.

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EFFECTS OF ACIDIFICATION ON THE BIOTA OF FRESHWATER ECOSYSTEMS

Jouko Sarvala
Departament of Biology
University of Turku
FIN-20500 Turku, Finland

1 INTRODUCTION

Acidification of terrestrial and freshwater systems, caused by air-borne pollutants, has been recognized as an acute environmental problem in many northern industrialized countries during the latest decades (e.g. Schindler 1988). Several studies have documented the biological characteristics of lakes at different pH levels (in Canada e.g. Roff and Kwiatkowski 1977, in Norway e.g. Wright et al. 1976, Raddum and Fjellheim 1984, in Sweden e.g. Almer et al 1974, in USA e.g. Brezonik et al. 1984), but the long-term temporal development of lake acidification has only seldom been followed (e.g. Nilssen 1980 in Norway and Morling and Pejler 1990 in Sweden). However, some unique whole-lake experiments have been conducted (Schindler et al. 1985 in Canada), and short-term enclosure experiments have been more common (e.g. Havens and DeCosta 1987).

In Finland, a comprehensive research program on the acidification problems, HAPRO, was funded by the Finnish government from 1985 to 1990 (Kauppi et al. 1990). Freshwater HAPRO involved a survey of biotic status in relation to pH and other lake water characteristics in 146 small forest lakes in South and Central Finland. The historical aspects of acidification were assessed with paleolimnological methods in 30 lakes (Huttunen et al. 1990). Here I shall briefly review the main results of HAPRO on the biotic effects of acid precipitation on freshwater ecosystems, complemented with results from earlier experimental work at Lammi Biological Station (Arvola et al. 1986). I shall not deal with the fish studies that are described by Rask (this volume); for the paleolimnological studies, see Huttunen et al. (1990).

2 BIOTIC EFFECTS OF ACIDIFICATION

Acidification may influence freshwater biota in three main ways. First, acidity may have direct toxic effects, e.g. by interfereing with calcium uptake of organisms. Such acid stress may lead to the death of the individual organism or, more often, prevent normal reproduction; the youngest stages are usually the most sensitive to perturbations. Second, acidification may have indirect effects mediated through biotic interactions (e.g. competition or predation) within the food web. Some organisms are more sensitive than others, and the ensuing changes in community structure can disrupt the previous balance between species. Third, acidification may have indirect effects mediated through biogeochemical cycles. Acidification changes water chemistry in lakes and streams both directly and indirectly as a consequence of changes in the soil chemistry of the drainage area. The chemical changes are then finally reflected in the biota.

2.1 Macrophytes

Macrophytic vegetation was thoroughly studied in 71 lakes and surveyed in an additional 64 lakes (Heitto 1990). The species composition in acidic lakes differed from the flora of more neutral lakes, but this could more often be attributed to differences in morphometry and trophic state than to pH. However, the number of macrophyte species decreased with increasing acidity. Also, the first axis of a DCA ordination of the study lakes based on the macrophyte species had the strongest correlations with pH, alkalinity and base cations. Correlations with the characteristics of the drainage area (e.g. proportion of exposed bedrock, which indicates sensitivity to acidification) were also significant. *Sphagnum* mosses, which utilize carbon dioxide as their carbon source, had invaded a few of the more acidic lakes. Otherwise no other species were found to clearly prefer acidic conditions. *Juncus bulbosus*, elsewhere reported as a typical acidophilous species, was only found in a single very acidic lake. Most elodeids were lacking in acidic lakes, and *Myriophyllum alterniflorum* probably has suffered from difficulties in carbon availability in acidic lakes. Possible changes in the occurrence of isoetids could not be assessed. Helophytes did not suffer from acidity but clearly favoured eutrophic conditions.

2.2 Phytoplankton and bacterioplankton

Acidity as such has little influence on the phytoplankton primary production or on the bacterial metabolic rates in lakes (Schindler 1988), although enclosure experiments often show a decrease in these rates, as well as in chlorophyll *a* and bacterial numbers at extremely low pH (e.g. Arvola et al. 1986). Decreased primary production observed in some acidified lakes has been connected with decreased phosphorus inputs from the acidified drainage area (Jansson et al. 1986). The discrepancy between enclosure experiments and events in the whole lake is explained by changes in community structure. Acidification may drastically change the taxonomic composition of phytoplankton.

Total phytoplankton biomass in the HAPRO lakes was mainly dependent on the total phosphorus and nitrogen levels, as well as on the water colour (humic content), with pH having a minor role (Kippo-Edlund and Heitto 1990). However, the occurrence of certain taxa was clearly dependent on pH. *Peridinium inconspicuum* was typical of acidic lakes, and dinophyceans, in general, increased with decreasing pH, while chlorophytes decreased. These trends were most pronounced in clear-water lakes. Sediment surface samples showed that euplanktonic diatoms were especially sensitive to acidification (Huttunen and Turkia 1990). Species numbers decreased from 30–41 taxa at high pH to 10–30 taxa at low pH, and in the most acidic lake group from about 30 taxa in brown waters to about 10 taxa in clear waters (Kippo-Edlund and Heitto 1990). A similar decrease in the number of phytoplankton taxa with decreasing pH was found in experimental enclosures by Arvola et al. (1986). A detrended correspondence analysis (DCA) based on phytoplankton species arranged the HAPRO lakes roughly according to autumn water pH. The first DCA axis showed a highly significant correlation (0.67^{***}) with pH and lower, yet significant, correlations with total phosphorus and nitrogen.

2.3 Periphytic diatoms

Periphytic communities in the littoral zone are the first to receive the acidic runoff from the close surroundings, and might, therefore, be expected to respond rapidly to acidification. Periphyton contains a large number of diatom species which are relatively easy to study. On the other hand, quantitative assessment of periphytic communities is extremely difficult. The littoral areas consist of a mosaic of various microhabitats with their characteristic periphyton, thereby increasing the difficulty of representative sampling. A periphyton sample may better reflect the quality of the local microenvironment than the state of the whole lake. Moreover, the grazing activities of macroscopic and microscopic littoral animals may have a decisive impact on periphytic algae. However, in spite of these confusing factors, some general trends could be observed in the periphyton of HAPRO lakes (Eloranta 1990). The number of diatom taxa decreased with decreasing pH from about 50 species in neutral lakes to about 20 species in the most acidic group (pH < 5.2). When the lakes were classified with a multiple discriminant analysis according to their periphytic diatom flora, the resulting lake groups correlated with the observed pH of lake water. When the lakes were grouped according to their humic content (total organic carbon [TOC]) and alkalinity, the number of species in each TOC group was always higher in lakes with higher alkalinity, while within each alkalinity group the number of species was highest in mesohumic lakes. The measured summer pH could be satisfactorily predicted ($r^2 = 0.54$) from the periphytic diatoms with a multiple linear regression equation; there was also a close correlation with the pH predicted from diatoms in sediment surface samples.

2.4 Crustacean zooplankton

Crustacean zooplankton abundance in 138 HAPRO lakes decreased with decreasing pH, but increased with increasing humus (TOC) content (Sarvala and Halsinaho 1990). Zooplankton was most abundant in shallow lakes. In a stepwise multiple regression analysis the most important variables explaining zooplankton abundance were TOC (30%), depth (10%), pH (2%) and colour (1%). The observed number of species was mostly dependent on the number of individuals studied, i.e. sample size. Because the sample volume was constant throughout the study, the sample size in terms of individuals was dependent on the abundance of crustaceans in the lake. Acidity also influenced crustacean diversity: in a stepwise multiple regression analysis the sample size explained 49%, pH 4%, depth 3%, TOC 2%, total organic nitrogen 2% and sulphate 1% of the observed number of species. Arvola et al. (1986) also reported a clear decrease in the number of rotifer and crustacean taxa with increasing acidity in their experimental enclosures.

There were faunal changes along with acidity changes in the zooplankton of HAPRO lakes (Sarvala and Halsinaho 1990). The calanoid and *Daphnia* species declined with increasing acidity, and littoral species were encountered in some samples. Zooplankton based ordination or classification analyses of the lakes did not distinguish the most acidic lakes as a separate group. However, the simultaneous comparison of the species and environmental data in a canonical correspondence analysis (CCA and detrended CCA) showed that the effect of pH on the crustacean fauna was statistically significant, although of minor magnitude. Other significant environmental factors were labile aluminium concentration, conductivity (or calcium), total organic carbon and total phosphorus. The first CCA or DCA axis represented acidity and the second axis was a combination of humic influence and nutrient level. Thus, although the abundance and species diversity of crustacean zooplankton in the HAPRO lakes were significantly related to acidity, the environmental parameters could explain only a minor fraction of the total variation. Partly this was certainly due to the sampling strategy based on single water columns in each lake. However, the weak relationships of the crustacean communities with the environment must have been partly due to the prevalence of direct and indirect biotic interactions in the ecology of zooplankton.

2.5 Lake macrozoobenthos

The abundance and biomass of macrozoobenthos in the 140 HAPRO lakes did not correlate with pH (Meriläinen and Hynynen 1990). The number of species (in all > 200) decreased with decreasing pH in the littoral zone ($r = 0.54^{***}$), but in the profundal the oxygen conditions and the general trophic state were most important. The littoral benthic fauna was thus more informative with respect to acidification. The littoral fauna could be most effectively sampled with the qualitative hand-net method. The first axis of a DCA ordination of the lakes correlated with pH and the second axis with soil characteristics of the drainage area. In accordance with earlier studies in other countries, certain species were found to be sensitive to acidification. The occurrence of these species was closely related to minimum pH. The most sensitive groups were gastropods, small mussels and larvae of Ephemeroptera; yet, *Leptophlebia* spp. and certain *Pisidium* species were among the most resistant species. Species numbers also decreased with decreasing pH in Chironomidae and Oligochaeta. Many insect larvae (often large-sized taxa such as Odonata, Trichoptera and *Sialis*, but also several smaller forms as some Chironomidae and *Chaoborus*) were very resistant to acidity, probably due to their impermeable cuticle. Fish predation (or the lack of predation in the most acidic lakes) may be an important regulator of these large invertebrates.

2.6 Stream macrozoobenthos

The distribution of benthic invertebrates was studied in relation to acidity in 54 streams (Hämäläinen and Huttunen 1990). The number of species was directly correlated with pH ($r = 0.74^{***}$), and an especially strong decline was observed at pH<5.0. In each pH class more species were observed in more humic waters. Tolerance limits were established for each species. Few species were very sensitive to acidification. Among the more sensitive were gastropods, small mussels, most Ephemeroptera larvae and certain caddisfly larvae (*Silo pallipes, Lype* spp., *Polycentropus irroratus, Sericostoma personatum, Hydropsyche angustipennis*). Several other species, even in the same groups, were found to be tolerant of acid conditions (*Leptophlebia* spp. among the Ephemeroptera, the plecopterans *Leuctra nigra, Nemourella picteti* and *Nemoura cinerea* and the trichopteran *Plectrocnemia* *conspersa*). The species optima and tolerances with respect to pH were also determined using weighted averaging and maximum likelihood methods. The minimum pH of stream water could then be predicted from the faunal composition of benthic samples. The minimum surface pH of a lake can thus be assessed by sampling the lake outlet of invertebrate assemblages.

3 FINAL REMARKS

Severe acidification decreases species diversity in all groups of aquatic organisms. Strong acidification also decreases the abundance and biomass of most groups, and may impede metabolic processes. High humus content seems to partly alleviate the negative effects of acidity.

Slight acidification mainly brings about changes in species composition of aquatic communities. Often the influence of slight acidification is indirect, usually through changes in food availability or predation risk. Although most of our common aquatic species are moderately resistant to slight acidity, the most sensitive species start to disappear at a relatively high pH, and this may have far-reaching consequences through the food web. The disappearance of fish has an especially dramatic influence on other organisms. Slight differences in the characteristics of individual species and populations may cause differences in responses to acidification between single waterbodies and between larger areas.

Probably the most serious consequences of acidification are the possibly irreversible or at least very slowly reversible changes in the soil biogeochemistry of the drainage area that can lead to large, long-term alterations in the biology of lakes and streams. Such changes may involve decreasing phosphorus input, increasing humic inputs and increasing mobilization of toxic heavy metals.

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ZOOPLANKTON AND MACROBENTHOS IN SMALL ACIDIC LAKES OF SOUTH KARELIA

Ryabinkin, A.V. and Vlasova, L.I.
Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute

185003 Petrozavodsk
Urickogo 50
Russia, Republic of Karelia

1 INTRODUCTION

There is an urgent need to investigate the effect of various aspects of acidification on the structure and dynamics of the functioning of aquatic communities in connection with increasing acidic contamination of fresh waters, deterioration of water quality, degradation of biocenoses and reduced bioproductivity during the last decades. First, the problem attracted the attention of the scientists in USA, Canada and Scandinavia where the degree of anthropogenic acidification was significant (eg. Forsberg 1989; Johansson and Nyberg 1981; Overrein et al. 1980; Dickson 1975; Hall and Ide 1987; Mierle et al. 1986; Abrahamsen et al. 1989, etc.). Finnish researchers have, in detail, investigated the results of anthropogenic acidification of fresh waters during the last 10 - 15 years (Haapala et al. 1975; Kämäri 1985; Kenttämies et al. 1985; Rask et al. 1986; Oksanen et al. 1988; Meriläinen 1988; Kämäri et al. 1991). Until now, in Russia, the investigations of acidification processes with their resultant changes in biota have been inadequate and irregular, despite previous knowledge of the principle mechanisms of how aquatic organisms react to changes in acidity (Skadovskiy 1928, 1955). Salazkin (1976) showed from the example of numerous lakes in the humid zone in USSR that decreased pH-values reduced species diversity and productivity of zooplankton and benthic communities.

In Karelia, the problem of acidification of surface waters has become most evident during the last 10 - 15 years (Abakumov 1986). Surface waters of Karelia are characterized by extremely low mineral content (average 25 mg l^{-1}) and by low alkalinity resulting in an insignificant buffering capacity and low resistance to acid stress. Atmospheric precipitation over the Karelian territory is consistently acidic with significant sulphate, nitrate and ammonium content. This can be a dangerous source of acid contamination of natural waters.

The aim of our research was to assess the present state of zooplankton and benthic communities in some highly clear water lakes of southern Karelia characterized by different pH-values.

2 MATERIAL AND METHODS

The investigations were carried out in four oligotrophic lakes having highly transparent water and a low mineral content during 1985 – 1990. Lakes with a small catchment area and prevailing atmospheric supply were selected. The pH–level of the lakes ranged from weakly acidic (Lake Uros) to acidic (Lake Golubaya Lamba). The main characteristics of the lakes are presented in Table 1.

Table 1. Main chemical and hydrological characteristics of the lakes examined.

Lake	Lake area km^2	Drainage area km^2	Mean depth m	Maximum depth m	Total ions mg l^{-1}	Colour grad Pt–Co	pH
Golubaya Lamba	0.037	0.382	4.3	8.0	7.1	2	5.0
Chuchyarvi	1.12	4.63	4.6	13.5	5.1	12	5.1
Lizhmenskoye	4.67	18.0	8.5	21.0	12.6	17	6.3
Uros	4.26	9.90	2.8	9.5	15.0	6	6.5

Zooplankton samples were collected using a Dzhedi net with an inlet diameter of 0.174 m. The layers of 0 – 2 m, 2 – 5 m, 5 – 10 m, 10 – 15 m and 15 – 20 m were sampled.

In the littoral zone 100 l of water was screened. Samples were preserved in a solution of 4 % formalin. The samples were counted in the laboratory using Bogorov counting cell and microscopes and recounted per m^3. Weight coefficients (wet formalin weight) were used to calculate biomass. The coefficients were taken from literature.

Macrobenthos from deep parts of the lakes were sampled using an Ekman grab (grabbing area 225 cm^2), those in the littoral zone using a hand net. The samples were sieved through a 0.5–mm mesh and preserved in 4 % formalin. The organisms were distributed into systematic groups and the species were identified in the laboratory. Each group was weighed to the nearest 0.0005 g. Number and biomass were recounted per m^2.

3 RESULTS

3.1 Zooplankton

Zooplankton communities of the four lakes examined were found to consist of 35 species: Copepoda (11 species), Cladocera (16 species) and Rotatoria (8 species; Appendix 1).

In oligoacidic lakes (Lake Lishmenskoye, Lake Uros), Copepods (*Eudiaptomus gracilis, Heterocope appendiculata, Mesocyclops oithonoides*) and *Cladocera* (*Daphnia cristata, Bosmina obtusirostris*) were dominant. Zooplankton consisted of 26 species. The average quantitative parameters are given in Table 2.

Species diversity of zooplankton in Lake Chuchyarvi and Lake Golubaya Lamba was low. Only 21 species of crustaceans and rotifers were found in these lakes, in which *Bosmina obtusirostris* predominated. Less abundant were *Mesocyclops leuckarti* and *Eudiaptomus* (the latter were found singly in Lake Golubaya Lamba). In the littoral zone of Lake Chuchyarvi, rotifers prevailed at some stations (among them were *Kellicottia* and *Conochilus*). Some researchers pointed out that acid-resistant species can flourish due to decreased competitive ability of acid-sensitive species. This fact was confirmed by the example of the small Lake Golubaya Lamba where the number and biomass of zooplankton were relatively high in 1987 - 1988 (44 500 and 61 100 ind. m^{-3}, 3.2 and 3.0 g m^{-3}, respectively), and where *Bosmina obtusirostris* predominated (more than 90 %) (Table 2).

Table 2. Number and biomass of zooplankton in the lakes examined (August, 1990).

Group of zooplanktonic organisms	Lake Uros		Lake Lishmenskoye		Lake Chuchyarvi		Lake Golubaya Lamba	
	ind m^{-3}	g m^{-3}	ind m^{-3}	g m^{-3}	ind m^{-3}	g m^{-3}	ind m^{-3}	g m^{-3}
Copepoda	3.5	0.25	13.5	0.14	2.5	0.05	-	-
Cladocera	3.1	0.26	2.1	0.14	2.7	0.09	0.8	0.03
Rotatoria	0.7	0.01	1.6	0.01	0.9	0.01	-	-
Total	7.3	0.52	17.2	0.28	6.1	0.14	0.8	0.03

3.2 Macrozoobenthos

Macrozoobenthos of the lakes investigated consisted of 35 species and groups of invertebrates (Appendix 2). The fauna of chironomids was the most diverse (20 species and larval forms). Species diversity in the lakes with pH of 5.0 - 5.1 (Lake Golubaya Lamba, Lake Chuchyarvi) essentially differed from that of the lakes with pH of 6.3 - 6.5. Molluscs, leeches, caddies flies, mayflies and some other groups of organisms were lacking in highly acidic lakes or were present singly, whereas they were abundant in weakly acidic lakes. The predominant group, Chironomidae, was represented exclusively by eurybiotic forms: *Chironomus* sp., *Stictochironomus crassiforseps*, *Procladius* sp., *Trissocladius zalutschicola*, *Cryptocladopelma viridula*, *Psectocladius* sp., and *Cricotopus* sp. Small *Tanytarsini* specimens (*Tanytarsus sp.*, *Cladotanytarsus sp.*) predominated in weakly acidic lakes.

It was noted that the total number of organisms caught was greater when using the hand net as opposed to the Ekman grab (see also Meriläinen and Hynynen 1990). Therefore it is preferable to use a hand net.

Number and biomass of benthic invertebrates greatly varied according to seasons, being somewhat lower in the lakes with pH of 5.0 – 5.1 compared to the lakes with pH of 6.3 – 6.5 (Table 3).

Interesting annual dynamics of the number and biomass of macrobenthos were observed in Lake Golubaya Lamba in 1985 – 1990 (Table 4; the data are given for August – September). A distinct trend towards the decrease of productivity of benthos was observed. In 1985 the biomass of the lake was 31.2 g m^{-2} due to intensive development of *Chironomus sp.* In the following years the biomass was substantially lower and *Chironomus sp.* was found only singly. There is no valid explanation of this phenomenon, but it is known that acidity had not changed during this period.

Table 3. Characteristics of benthic communities in lakes with different degrees of acidity.

Lake	pH	Number of species and groups	Number of Chironomidae species	Chironomidae		Oligochaeta		Mollusca		Total	
				ind m^{-2}	g m^{-2}	ind m^{-2}	g m^{-2}	ind m^{-2}	g m^{-2}	ind m^{-2}	g m^{-2}
Uros	6.3	32	19	440	0.73	267	0.05	22	0.02	729	0.80
Lishmenskoye	6.5	21	18	1 187	0.59	111	0.02	355	0.24	2353	0.85
Chuchyarvi	5.1	10	7	311	0.10	29	0.01	-	-	340	0.11
Golubaya Lamba	5.0	12	4	44	0.29	-	-	-	-	44	0.29

Table 4. Number and biomass of zooplankton and benthic organisms in Lake Golubaya Lamba (August-September).

Year	1985	1987	1988	1989	1990
Zooplankton					
ind m^{-3}	-	44.5	61.1	-	0.8
g m^{-3}	-	3.2	3.0	-	0.03
Macrobenthos					
ind m^{-2}	11 721	2 708	1 598	111	44
g m^{-2}	31.3	2.95	1.10	0.40	0.29

4 DISCUSSION

Both resistance of some ecosystem elements and interspecies relations in aquatic biocenoses should be taken into account considering the effect of acidification on functional structure and dynamics. The resistance of some species to the effect of pH, which is one of the main parameters of acidification, results from their adaptive ability formed during the evolution of the population. For this purpose experimental laboratory and field investigations are used, as well as methods of establishing thresholds of sensitivity of individual species and groups of organisms according to the results of field observations in the lakes with different pH, revealing an ecological spectrum of the sensitivity of aquatic organisms. The sensitivity threshold is an estimate of the pH at which species are found in nature. We preferred the latter for our work.

Zooplankton and particularly zoobenthos are reliable indicators for monitoring assessment. Having an ability of physical and functional cumulation, they may serve as integral indicators of the long-term state of a lake and in some cases may be used instead of a series of physical and chemical observations.

At present it is well known that acidification of lakes results in a distinct trend to impoverishment of species composition of both zooplankton (eg. Nilssen et al. 1984, Stenson 1985, Sarvala and Halsinaho 1990) and zoobenthos.

Species diversity in some lakes of Canada was shown to be 1.7 times lower at pH of 4.4 compared to that at pH of 6.0 – 6.5 due to the low occurence of Ephemerophere, amphipods and Ceratopogonidae in acidic waters (Harvey and McArdle 1986). Similar results were obtained for 55 lakes in Finland (Kenttämies et al. 1985). From the example of a great number of lakes in North–Western USSR it was shown that the amount of zoobenthic species decreased from 400 in neutral–alkaline lakes to 200 in oligoacidic, and to 15 – 20 in polyacidic lakes (Salazkin 1976). The most acid-sensitive species and groups of organisms disappear first from biocenoses. Among zooplanktonic species the most acid–sensitive are Cladocera, while the most acid-resistant are Rotatoria. In lakes with pH below 6.0, molluscs with limestone shells suffer most severely. Gastropoda are practically eliminated at pH below 5.0, and at pH below 4.5 most species of *Bivalia* are not found. Higher crustaceans are particularly acid–sensitive, *Gammarus lacustris* and *Pallasea quadrispinosa* are not found at pH below 5.5, *Mysis relicta* at pH of 5.8, and *Asellus aquaticus* at pH of 6.1 (Wiederholm and Ericksson 1977).

There are marked differences in tolerance range among species of closely related taxa, therefore estimates should be made at the species level. Thus a wide range of pH 3.5 to 5.5 and higher was shown to induce a significant difference in resistance of mayfly species in some Swedish rivers (Engblom and Lingdell 1984). At the same time it was noted that decreased acidity influenced the occurrence and distribution of many eurybiotic species due to interspecies competition. In acidic lakes, pressure by planktivores and benthophages is greatly reduced due to the absence of many fish species resulting in a shift in size structure of the community towards the development of larger individuals normally consumed in neutral lakes.

Individual sensitivity, trophic competition and changes in predator pressure determine the structure and development of aquatic species in acidic waters. Productivity of acidic lakes is often higher than that of neutral lakes due to rapid development of species maximally adapted to acid stress.

5 CONCLUSIONS

The results obtained using field data from some highly clear water lakes of southern Karelia with pH of 5.0 – 6.5 revealed some regularities in dynamics of structural and functional changes in zooplankton and benthos communities induced by acid stress. Our results in general are in agreement with the data from literature.

1. Considerable decrease in species diversity of zooplankton and benthos communities were observed due to an increase in acidity.

2. A number of acid-sensitive species and groups of organisms were absent from acidic lakes: molluscs and many species of Cladocera, Ephemeroptera and *Trichoptera*.

3. Predominant species of zooplankton in acidic lakes were *Bosmina obtusirostris, Mesocyclops oithonoides, M. leuckarti*, and Rotatoria.

4. Chironomidae (*Procladius* sp., *Trissocladius zalutschicola*, *Chironomus*), Ceratopogonidae and Hydrachnellae predominated in benthic communities.

5. No distinct dependence of number and biomass upon the degree of acidity was found. Occasionally the biomass of acidic lakes can be rather large due to increased development of adapted species (*Bosmina obtusirostris*, *Chironomus*, etc.) and due to lack of competition and decreased predator pressure.

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APPENDIX 1. ZOOPLANKTON SPECIES AND GROUPS OF THE DIFFERENT ACIDIFIED LAKES.

	Lake Golubaya Lamba	Lake Chych-yarvi	Lake Lishmen-skoye	Lake Uros
COPEPODA				
Eudiaptomus graciloides Lill.	-	-	+	+
E. gracilis Sars	+	+	-	-
Heterocope appendiculata Sars	-	-	+	+
Cyclops strenuus Fisch.	+	+	+	-
C. scutifer Claus	-	+	+	-
Cyclops sp.	-	+	+	-
Acanthocyclops vernalis (Fisch.)	-	-	+	-
Acanthocyclops sp.	+	-	-	-
Mesocyclops leuckarti claus	+	+	-	-
M. oithonoides Sars	-	+	+	-
M. crassus (Fisch)	-	-	+	-
CLADOCERA				
Sida crystallina	-	+	-	+
Limnosida frontosa Sars	-	-	+	-
Holopedium gibberum Zaddach	-	-	+	+
Daphnia longispina (O.F. Müller)	+	-	-	+
D. cristata Sars	-	-	+	+
Ceriodaphnia quadrangula (O.F.Müller)	+	-	-	-
Scapholeberis mucronata (O.F. Müller)	-	-	+	-
Alonopsis elongata Sars	+	+	-	-
Chydorus sphaericus (O.F. Müller)	+	+	-	-
Rhynchotalona falcata (Sara)	-	+	-	-
Alona affinis Leydig	+	-	-	+
Bosmina obtusirostris Sars	+	+	+	+
B. coregoni Baird	-	-	+	-
Polyphemus pediculus (Linne)	+	+	-	+
Bythotrephes longimanus Leydig	-	-	+	-
Leptodora kindtii Lill.	-	+	-	+
ROTATORIA				
Polyarthra sp.	-	-	+	-
Euchlanis sp.	-	-	-	+
Asplanchna priodonta Gosse	-	+	+	+
Keratella cochlearis (Gosse)	-	-	+	-
Kellicottia longispina (Kellicott)	+	+	+	-
Conochilus hippocrepis (Schrank)	-	+	-	-
C. unicornis Rousselet	-	+	+	+
Bipalpus hudsoni Imhof	-	-	+	-

APPENDIX 2. SPECIES AND GROUPS OF MACROINVERTEBRATES OF THE STUDIED LAKES.

	Lake Golubaya Lamba	Lake Chych-yarvi	Lake Lishmen-skoye	Lake Uros
Nematoda	+	–	+	+
Gastropoda	–	–	–	+
Sphaeridae	–	–	+	+
Oligochaeta	+	+	+	+
Hirudinea	–	–	+	+
Helobdella octoculata L	–	–	–	+
Hydrachnellae	+	+	–	+
Ephemeroptera	+	–	+	+
Heptagenia fuscogrisea	–	–	+	–
Odonata	+	–	–	+
Megaloptera	–	–	+	+
Sialis flavelatera	+	–	–	–
Trichoptera	+	–	–	+
Phryganea striata	–	–	–	+
Mystacides azurea	–	–	–	+
Molanna angustata	–	–	+	–
Coleoptera	+	–	+	+
Diptera				
Chironomidae	–	–	–	+
Tanypodinae				
Procladius sp.	+	+	+	+
Orthocladiinae				
Trissocladius zalutschicola (Lipina)	–	+	+	+
T. potamophilus (Tshernov)	–	–	–	+
Psectrocladius sp. (3 luge)	+	+	–	–
Cricotopus sp.	+	+	–	–
Chironominae				
Chironomini				
Cryptocladopelma viridula (Fabr.)	–	–	–	+
Polypedilum scalaenum (Schrank)	–	–	–	+
P. bicrenatum Kieff	–	–	–	+
Pagastiella orophila (Edw.)	–	–	–	+
Chironomus sp. Mg	+	–	–	–
Sergentia longiventris Kieff	–	+	+	+
Stictochironomus crassiforseps (Kieff)	–	+	+	+
Microtendipes pedelus (De Geer)	–	–	–	+
Pseudochironomus prasinatus Staeg.	–	+	–	+
Limnochironomus nervosus Staeger	–	–	–	+
Tanytarsini				
Tanytarsus sp. Van der Wulp	–	–	+	+
Cladotanytarsus sp. Kieff.	–	–	–	+
Ceratopogonidae	+	+	+	+
Tabanidae	–	–	–	+

THE EFFECTS OF ACID DEPOSITION ON FISH POPULATIONS OF SMALL LAKES IN FINLAND

Martti Rask

Finnish Game and Fisheries Research Institute
Evo State Fisheries and Aquaculture Research Station
FIN-16970 Evo
Finland

1 ABSTRACT

A fish status survey of 80 acid sensitive lakes showed that acidification has affected the fish populations in small Finnish lakes. Changes in the structure of roach populations were quite common. In some of the most acidified and aluminium rich lakes also affected perch populations were affected resulting in low amount of fish that were large and old. Increased growth rates of fish were also found in some lakes probably due to decreased food competition.

The observations on the decreased population densities of perch in the fish status survey were ascertained using mark and recapture studies of some perch populations. The spawning of perch in some acidified lakes was delayed and the survival of developing embryos was low, suggesting that reproduction failure was the major reason for the decrease of the populations. Increased mortality of adult perch was recorded in a few cases.

Whitefish stocking seems to be a suitable method in mitigating the acidification effects on fisheries. A small scale monitoring of liming effects on fish status of lakes began in the late 1980's. Two more detailed lake liming studies are presently underway.

2 INTRODUCTION

Acidification of lakes through increased sulphur and nitrogen emissions has resulted in considerable losses of fish populations in Norway (Henriksen et al. 1989) and Sweden (Hultberg 1985). In addition, observations concerning the harmful effects of acidification on fish have been made at least in the Netherlands (Leuven and Oyen 1987), United Kingdom (Turnpenny et al. 1988), France (Massabuau et al. 1987), Germany (Fischer-Scherl et al. 1986), U.S.A. (Schofield 1976), and Canada (Somers and Harvey 1984).

Although mass mortalities of adult fish have been observed, for example in Norwegian rivers (Leivestad and Muniz 1976; Henriksen et al. 1984), decreased recruitment of young fish has been considered the primary factor leading to the gradual extinction of fish in the acidified waters. The decreased recruitment may result from both lowered viability and survival of fertilized eggs, embryos and fry (Runn et al. 1977; Peterson et al. 1980; Rask 1983; Cleveland et al. 1986; Tuunainen et al. 1991) and impaired prespawning processes, e.g. maturation of gonadal products and related metabolic processes (Beamish et al. 1975; Tam and Payson 1986; Vuorinen et al. 1990).

In Finland a major research programme concerned with acidification (HAPRO) was started in 1985. Previously, little was known about the possible effects of acid precipitation on fish populations in Finnish lakes. The studies were carried out as a joint project of the Finnish Game and Fisheries Research Institute and the Lammi Biological Station of the University of Helsinki. The aim of this paper is to summarize the main findings of the fish status survey during 1985 - 1989 and to describe some of the recent research activities.

3 FISH STATUS SURVEY

3.1 The lakes

Lakes having a known acidification history were preferentially selected for the fish status survey (Rask & Tuunainen 1990). Among the 80 lakes of the survey, 25 had experienced acidification based on paleolimnological diatom analyses (Tolonen and Jaakkola 1983; Simola et al. 1985; Tolonen et al. 1986; Huttunen et al. 1990) or according to the chemical properties of water (Kämäri 1985).

More than half of the 80 lakes were located at a distance of less than 100 km from the south coast of Finland in an area where the mean annual sulphur deposition is the highest in Finland. Most of the lakes were small (Table 1), oligotrophic lakes with small forest catchments often characterized by thin soils and rocky landscapes but occasionally by glacialfluvial sand or gravel material.

Table 1. Some characteristics of lakes from the fish status survey.

	Mean	Range
Lake area, ha	22	1,0 - 194
Altitude above sea, m	97	16,0 - 218
pH	5,7	4,4 - 7,6
Alkalinity, mmol/l	0,05	0,0 - 0,37
Conductivity, mS/m	3,1	0,8 - 5,7
Colour, mg Pt/l	25	0,0 - 90
Ca, mmol/l	0,05	0,0 - 0,15
Total Al, µg/l	110	0,0 - 287
Labile Al, µg/l	48	0,0 - 138

3.2 Fish catches

Fish were sampled using a series of eight gill nets having mesh sizes ranging from 12 to 60 mm. Each lake was sampled one to five times at depths of 2 – 4 m (Rask & Tuunainen 1990). The total weights and the number of fish in the gill net catches varied widely. Some acidified lakes in the south coast seemed to be empty of fish, however, the largest catches were also from quite acidic lakes (Tuunainen et al. 1991). Therefore there was no statistically significant relationship between fish catches and water quality of the lakes (cf. Ranta et al. 1992).

There was a clear relationship between the number of fish species in the catches and the lake acidity. In the most acidic lakes with pH < 5.0, one or two species were encountered whereas in the more neutral lakes (pH > 6.0), the number of species was usually 3 – 5. Perch was present in almost all of the lakes. Roach, ruffe and pike were also common (Table 2). Altogether, 13 species of fish were captured during the fish status survey.

Table 2. The frequency of occurrence of different fish species (%) in 80 lakes based on gill net catches and the mean total catch of each species per gill net series. The whitefish are mostly stocked plankton whitefish; only two lakes had an original reproducing whitefish population. In addition, pikeperch (1 lake) and trout (2 lakes) were stocked.

Fish species	%	Total weight (g)	
		Mean	Range
Perch, *Perca fluviatilis*	96	4 803	213 – 31 809
Ruffe, *Gymnocephalus cernua*	49	318	8 – 1 780
Pike, *Esox lucius*	44	946	100 – 3 801
Roach, *Rutilus rutilus*	40	4 875	20 – 12 482
Whitefish, *Coregonus* sp.	23	1 523	124 – 12 167
Bream, *Abramis brama*	5	1 608	696 – 2 295
Dace, *Scardinius erythrophthalmus*	3	531	21 – 1 041
Bleak, *Alburnus alburnus*	3	47	21 – 72
Vendace, *Coregonus albula*	3	663	161 – 1 951
Trout, *Salmo trutta*	3	3 238	1 212 – 5 264
Crucian carp, *Carassius carassius*	1	326	
Burbot, *Lota lota*	1	673	237 – 1 297
Pikeperch, *Stizostedion lucioperca*	1	196	128 – 264

3.3 The structure of fish populations

3.3.1 Perch

Perch were caught in 77 out of 80 lakes covering a pH range of 4.4 – 7.6. Based on gill net catches, the perch populations were dominated by small and young fish in lakes having pH > 5.0 (Raitaniemi et al. 1988). In some of the lakes with pH < 5.0, the populations were dominated by larger fish (Fig. 1). The mean weight of perch in the lakes varied usually between 10 and 70 g but in some lakes with pH < 5.0 the mean weight of perch was greater than 100 g and in a few cases even more than 300 g. In these lakes the number of perch was usually low. The fish were also old, the mean age being over 7 years, whereas it was 3.9 years in the entire set of 80 lakes. Both the mean weight and the mean age of perch in the catches correlated significantly with the lake pH and with the aluminium concentrations in the water (Rask & Tuunainen 1990).

The catches of few, large individuals of perch in some acidified lakes were considered to be a consequence of severe reproduction failures (Raitaniemi et al. 1988). The high aluminium concentrations in these lakes (Fig. 2) support the observations on aluminium toxicity during acidification that have been reported in many studies (Baker & Schofield 1982; Henriksen et al 1984; Vuorinen et al. 1990; Tuunainen et al. 1991).

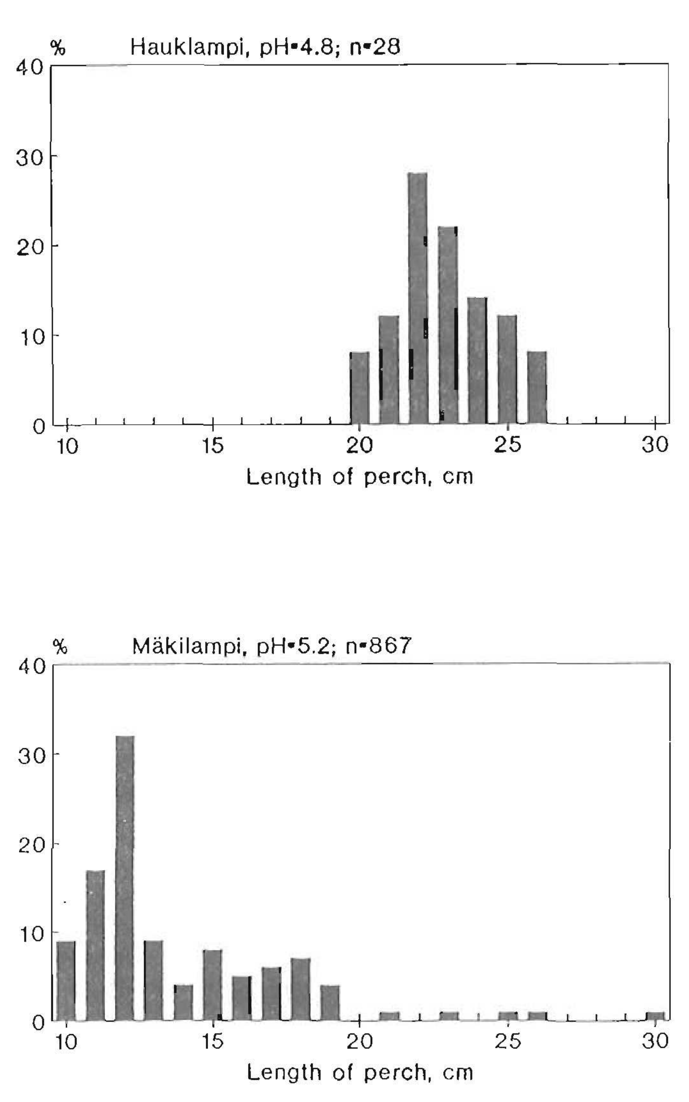

Fig. 1. The length frequency distribution of perch in a highly acidified lake (top) and in a less acidic lake (bottom). The absence of small perch is due to failures in reproduction (Tuunainen & al. 1991).

3.3.2 Roach

Roach were caught from 32 lakes at a pH range of 5.1 – 7.6. The lower limit pH of 5.1 for the occurrence of roach in the catches indicates that roach is far more sensitive to acidification than perch (Rask & Tuunainen 1990). The trend in the size and age distribution of roach catches was similar to that of perch: in neutral lakes the populations were dominated by small and young fish, whereas in the lakes with a pH less than 6.0, the fish tended to be larger and older (Fig. 3). The mean weight of roach in the catches varied from 11 to 560 g and the highest mean weights were recorded in lakes with pH < 6.0. The pH values of the two lakes where the mean age of roach in the catches exceeded 10 years were 5.1 and 5.5 (Rask & Tuunainen 1990).

Roach is probably the best indicator species of acidification among the Finnish fish fauna. This is because roach is widely distributed, common, well known, easily observed or caught, and because it is so sensitive to acidification (Rask 1989a).

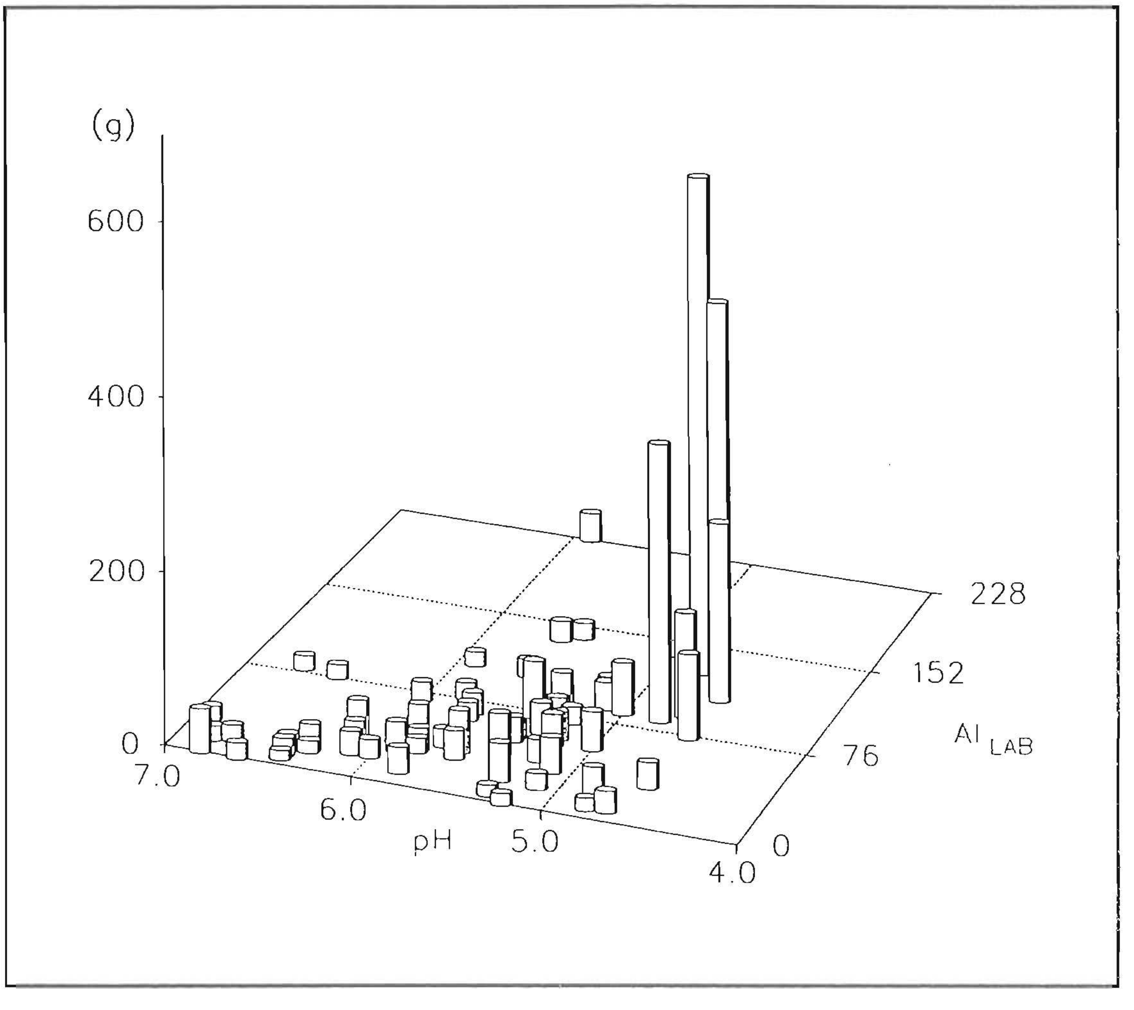

Fig. 2. The mean weight of perch (g) in the gill net catches from the fish status survey in relation to lake pH and the concentration of labile aluminium. The greatest mean weights of perch were found in acidic (pH < 5) lakes with high concentrations (75 – 150 µg/l) of labile aluminium, conditions where no successful reproduction of perch takes place (Tuunainen et al. 1991).

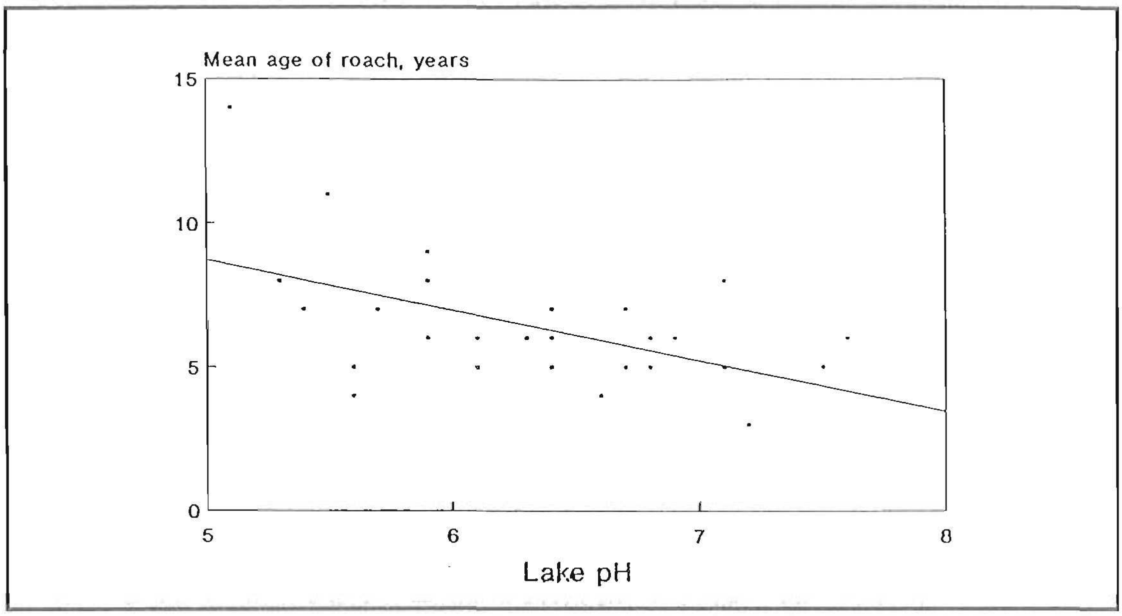

Fig. 3. The mean age of roach in gill net catches of the fish status survey in relation to lake pH. Low mean age indicates normal reproduction whereas high mean ages (round 10 years) suggest difficulties in reproduction.

3.4 Patterns in the growth of fish

3.4.1 Perch

The mean length of perch at the age of five years was usually 120 – 200 mm. In some cases 200 mm was exceeded and values more than 220 mm were found in five lakes with pH < 5.0. The correlation between length at age five and lake pH was significant (Rask & Tuunainen 1990). In a comparison of perch growth in different types of waters (Rask & Raitaniemi 1988) it was shown that the perch in some strongly acidified lakes grew more rapidly than in large lakes or coastal waters (Fig. 4) and was comparable to the pelagic predatory perch of large waters (Raitaniemi et al. 1988). The high growth rates in strongly acidified lakes has possibly arisen due to the decrease in intraspecific food competition. Since perch was the sole fish species of the lakes no interspecific competition took place.

3.4.2 Roach

The growth rate of roach was greater in acidic than in neutral lakes. The mean backcalculated length of roach at the age of 5 years ranged from 121 to 211 mm and the differences among lake groups having different pH values were statistically significant (Rask & Tuunainen 1990). As in the case of perch, the higher growth rates of roach in acidifying waters is considered to be a consequence of decreased competition for food in decreasing populations. However, in lakes of pH 5.0 – 6.0 where roach populations are decreasing, there are usually high numbers of perch present. Thus, although there may be no intraspecific food competition among the remaining roach, interspecific competition still occurs.

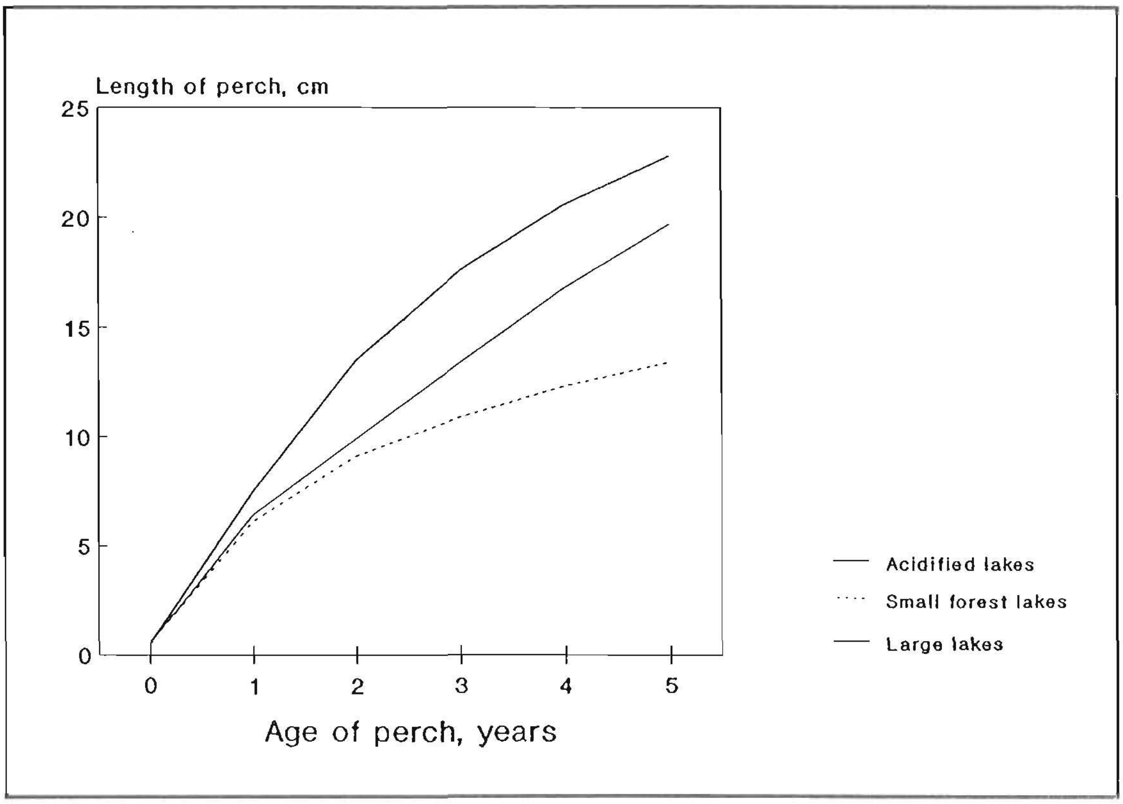

Fig. 4. Mean length at various ages of perch from five acidified lakes, three large lakes and the Baltic coast, and five small non-acidified, forest lakes. The high growth rates in the acidified lakes were thought to be due to decreased food competition in sparse populations (Rask & Raitaniemi 1988).

3.5 Acid induced mortality of adult fish

During the 1980's, we recorded increased mortality of adult perch in three lakes. In May 1981 dead perch were found in a strongly acidic, humic lake. Altogether 25 dead fish were recorded, however this was probably only a fraction of all dead fish. Thus the population of ca. 200 adult perch suffered a considerable loss (Rask 1984a). In May 1986 during a mark and recapture study of six perch populations (Lappalainen et al. 1988) dying adult fish were recorded in two lakes. In one of the lakes, blood and plasma samples were taken from the dying fish. The plasma Na and Cl concentrations were extremely low. Furthermore, the fish suffered from hypoxia due to decreased oxygen affinity of red blood cells (Nikinmaa, personal communication). In another lake a diver found four dead perch while doing an egg strand survey in late May 1986 (Lappalainen 1987).

The dying of adult perch took place in all three lakes during May. Probably the mortality was a joint effect of several reasons, such as acidity stress due to snow melt, increased metabolic rate in warmer water, and increased energy demands during reproduction. In all three lakes the perch populations have also suffered from decreased reproductive success due to high mortality of developing embryos. Thus, although the sudden death of adult fish may be fatal for a population, it seems that in Finnish lakes it is not the main reason for the acid induced decrease of fish populations.

4 PERCH POPULATIONS

The observations on the acidification effects of perch populations in some lakes during the fish status survey were ascertained in a mark and recapture study of six lakes (Lappalainen et al. 1988). The density of the populations in four acidified lakes were 0 – 260 perch per hectare while the densities in two less acidic reference lakes were 1430 and 3360 perch per hectare. The biomass of perch in the acidified lakes was 0 – 14 kg ha^{-1}, while in the control lakes it was 20 and 52 kg ha^{-1}. In a comparison of mark and recapture data from 12 lakes the trend was similar: densities and biomasses of perch were lower in acidified than in less acidic lakes (Table 3; Rask 1989b).

Table 3. The mean density and biomass of perch in six acidified and six less acid lakes. Data from Rask (1989).

	Density, ind ha^{-1}		Biomass, kg ha^{-1}	
	Mean	Range	Mean	Range
Lakes with pH < 5.0	260	0 – 1020	10	0 – 20
Lakes with pH > 5.0	1640	530 – 3360	27	12 – 52

Regular monitoring of two perch populations took place during the 1980's including an estimation of population size using the mark and recapture method every or every second year (Rask 1991). The length frequency distribution of the populations over time (years) shows a gradual decrease of the fish in the lakes and a shift towards the dominance of larger and older fish (Fig. 5).

5 REPRODUCTION OF PERCH

5.1 Mortality of developing embryos

Laboratory exposures of developing perch embryos to low pH showed remarkable mortalities of embryos at pH levels below 5.0 (Rask 1983). Rearing samples of fertilized perch eggs in their home lakes gave similar results (Lappalainen et al. 1988). The embryo mortality in the most acidified lake was close to 100 %, whereas in a circum neutral control lake the mortality was less than 5 %. In another series of field exposures the mortality of perch embryos was 10 % in a lake with pH 5.0 and varied from 25 to 100 % in lakes with pH < 5.0 (Tuunainen et al. 1991).

According to these observations it seems that the embryo mortality of perch starts to increase at pH levels of ca. 5. At pH levels of 4.5 mortality may increase to tens of percents and even to 100 %. This supports the suggestion that failures in reproduction are the main reason for acid induced damages in fish populations. In addition, newly hatched fish larvae are considered to be more acid sensitive than developing embryos

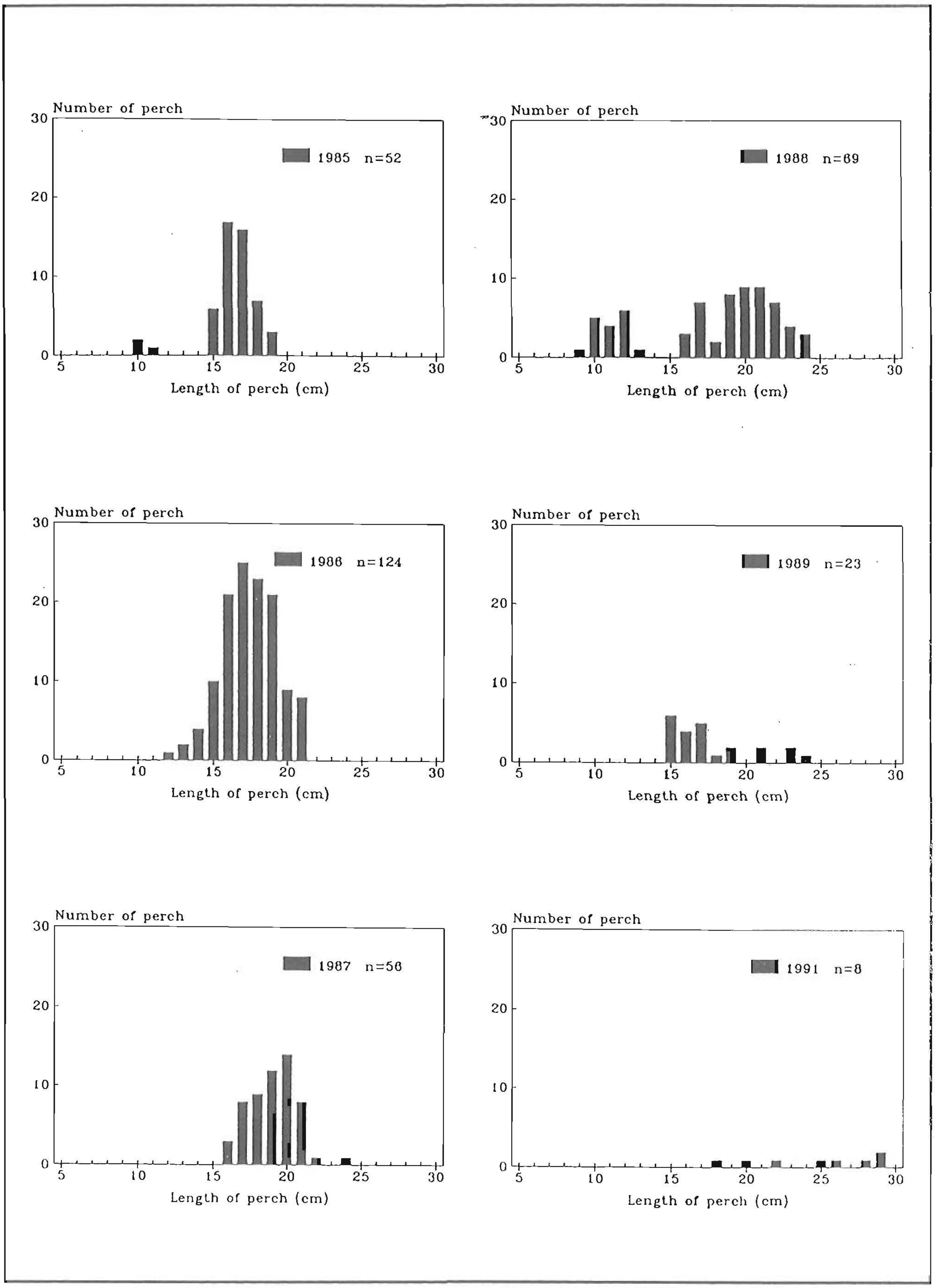

Fig. 5. The length frequency distributions of perch in a small (2.3 ha) lake in 1985 - 1991. During the 1980's the lake experienced rapid acidification from pH levels of ca. 5 to values of 4.5 and less, resulting in decreased or inhibited reproduction (Lappalainen et al. 1988).

(Rombough 1983, Rask 1984b). During our field exposures of perch embryos we felt that most of the perch larvae that hatched in the lakes, having pH < 5.0 and high aluminium concentration in the water, died soon after hatching.

5.2 The timing of spawning of perch in acidified lakes

During the fish status survey in 1985 some perch were caught that still had their gonad products present in midsummer, one month after their normal spawning time. Observations of delayed maturation of fish in acidic and aluminium rich waters were also made in laboratory exposures (Vuorinen et al. 1990). To study the effects of acidification on the timing of spawning in natural conditions, we carried out a field experiment using five perch lakes having various acidity levels (Rask et al. 1990). The examination of the maturity of 1440 male and 350 female perch throughout the spawning time indicated a clear delay in spawning in two of the most acidified lakes (pH 4.5 – 4.8) which also had the highest aluminium concentrations in the water. The delay was 100 – 150 degree days > 5 °C or 2 – 3 weeks. In two low aluminium lakes with pH 4.6 – 5.1 the spawning of perch occurred almost simultaneously with a circum neutral control lake (Rask et al. 1990).

These observations indicate that the maturation of gonads of fish can be affected by the acidification. Thus, the whole reproductive cycle of fishes should be taken into account when assessing the reason for acid induced reproduction failures.

6 MITIGATION OF THE EFFECTS

6.1 Stocking of lakes with acid tolerant fish species

The harmful effects of acidification on fisheries can be temporarily mitigated by stocking the lakes with fish species which are more tolerant of acidic conditions than the original fish fauna. In Finland stocking with whitefish is a common practice in fisheries management of small lakes (Salojärvi 1986). Whitefish were found in our fish status survey in 20 lakes in a pH range of 4.8 – 7.6 (Rask et al. 1988) indicating that whitefish is fairly acid tolerant. According to laboratory exposures of newly hatched larvae to low pH, the sensitivity of different species was as follows: roach > pikeperch > whitefish = perch > pike (Tuunainen et al. 1990).

In autumn 1986 six small lakes at different stages of acidification were stocked with one–summer–old whitefish. In two of the most acidified lakes the introduction failed: the fish did not survive, evidently due to high acidity and high aluminium concentrations of the lake waters. In one of the most acidified and aluminium rich lakes and in two less acidic lakes the introduction was successful. Three years after the stocking the mean weights of whitefish in these lakes were 580, 250 and 360 g, respectively. The reason for the highest mean weight of introduced whitefish in the most acidified lake was interpreted to be a good availability of food. This was thought to be due to the absence of other fish in that lake whereas in the less acidic lakes the whitefish probably felt interspecific food competition from the dense populations of perch (Rask et al. 1992). Plasma Na and Cl concentrations of whitefish in the most acidified lake were lower than in the less acidic lakes suggesting that despite the good feeding conditions and growth, the fish still experienced some acid stress in the most acidic lake.

These observations suggest that stocking with whitefish may be a good alternative in mitigating the acidification effects. Specifically, this may be the case at an early stage of acidification, down to pH levels of 5.0 – 5.5. In very acidic conditions, with pH permanently less than 5.0, neutralization of the water would be useful before stocking.

6.2 Neutralization of acidic lakes

Liming lakes and rivers is nowadays a common measure in temporary mitigation of acidification effects. Especially in Sweden where an operational liming programme was started in 1982 (Nyberg and Thornelof 1988), resulting in lime treatment for several thousands of lakes during the 1980's. In Finland the first liming experiments were done in the late 1960's to make some small acidic lakes more suitable for recreational fishing. Altogether some 100 – 150 lakes have been limed in Finland, but there is no public liming programme in the country against the acid precipitation.

We started a small scale monitoring of fish status in limed lakes in late 1980's. Liming of the lakes took place in 1986 – 1988 and the first post–liming fish status survey was carried out in 1989 (Raitaniemi & Rask 1990). No effects of liming were detected in catches or growth of perch in comparison to pre–liming conditions. The small roach populations remaining in some of the lakes prior to liming started to reproduce again, resulting in the occurrence of small roach in the gill net catches in 1989 (Fig. 6).

In recent years two multidisciplinary lake liming studies have been started in Finland. In one of these, the study area contains a chain of lakes and involves the use of different liming methods. In one of the lakes in the chain, fish and crayfish studies have been carried out since 1986. Fish species interactions, length and age distributions, growth patterns, diet and availability of benthic food for fish will be studied during the next five years.

In another experiment a lake was divided into two using a plastic curtain. One half of the lake was neutralized and the other will be a control (Weppling et al. 1992). The effects of liming will be studied on the plankton community and processes, benthic fauna and fish to see whether the changes in the metabolism of the lake result in more suitable conditions for fish (Rask 1991). In addition, the effects of liming on the Hg and Cs–137 concentrations of fish will be monitored.

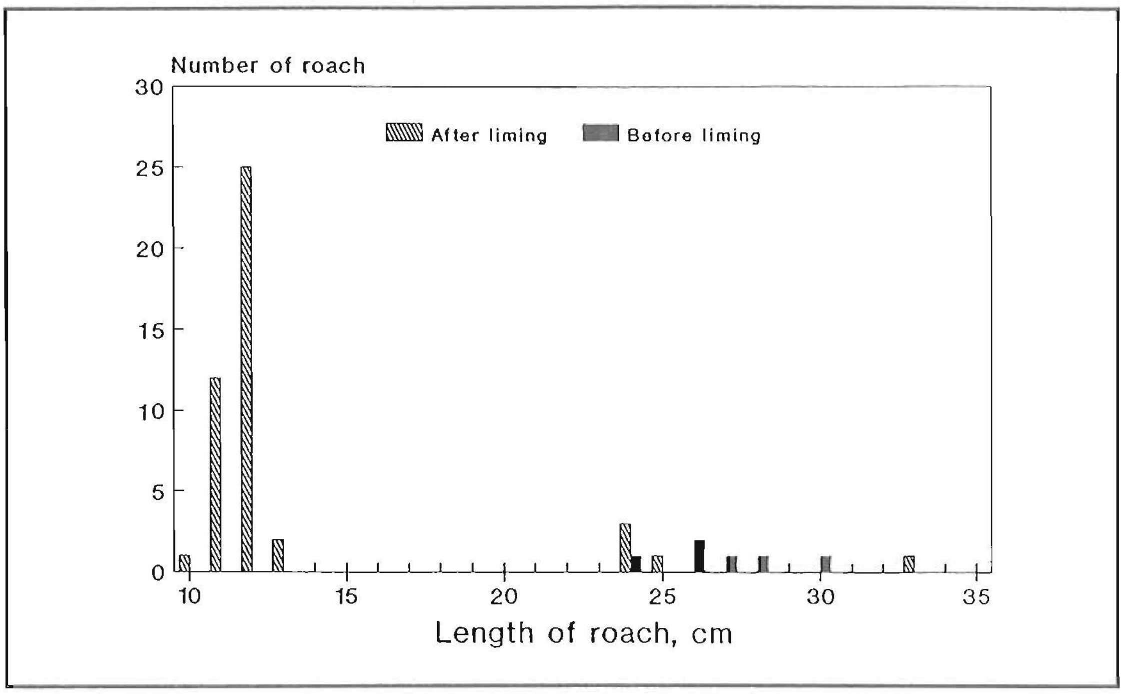

Fig. 6. The length frequency distribution of roach in an acidic lake before liming in 1986, and after liming in 1989. The few large and old roach present in the lake, reproduced successfully after liming resulting in the appearance of a new cohort (Raitaniemi & Rask 1990).

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THE CHARACTER OF THE ALGAL FLORA OF SOME OLIGOHUMIC LAKES OF SOUTH KARELIA WITH DIFFERENT DEGREES OF ACIDITY

Kalugin, A. I.

Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute

185003 Petrozavodsk
Urickogo 50
Russia, Republic of Karelia

1 MATERIAL AND METHODS

The quantitave samples of phytoplankton were taken by generally accepted methods at 2 – 5 stations, dependent on the area of the water body. The volume of the sample was one liter. Fixation was performed in two steps: an iodine solution, made from our own recipe, was directly added at the moment of sampling and 5 – 7 hours later formalin, up to a 1 % concentration, was added. Later the samples were concentrated using the settling method where filtration of the supersediment water was run through the filter, "Vladipor" N 9 (pore diameter 0.9 μm). The phytoplankton biomass was calculated using the mean value of the cell volume.

The species composition of periphyton and microphytobenthos and their abundance were investigated at 1 – 2 stations. If possible the following substrata: stone, dead wood, reed and *Lobelia* were studied up to a depth of 0.5 m. Fixation was the same as with phytoplankton. In all, analyses were conducted for 21 samples of phytoplankton, 11 samples of periphyton and 4 samples of microphytobenthos.

2 RESULTS

2.1 Lake Golubaya Lamba

In Lake Golybaya Lamba the total biomass of phytoplankton reached 0.5 mg l^{-1}. *Dinobryon cylindricum* and *Peridinium inconspicuum* were dominant. The accumulations of the filamentous algae remained present throughout the investigations and almost entirely covered the bottom. A small amount of *Aulacoseira (Melosira) granulata*, *A. ambigua*, and some desmidiales and benthic diatoms were also present (Table 1). The periphyton at the bottom of the water body and on the wood was formed by *Mougeotia* with other Zygnemales such as *Zygnema* and *Oedogonium* and also some filamentous Cyanophyta, eg. *Hapalosiphon*. In total the benthic and plankton samples yielded 32 species and forms of algae.

2.2 Lake Chjuchyarvi

Lake Chjuchyarvi contained the lowest phytoplankton biomass of the studied lakes, only 0.3 mg l^{-1}. The dominant species were *Peridinium inconspicuum, Dinobryon elegans, Gymnodinium sp.* and *Tabellaria quadriseptata*. In the hypolimnion (at a depth of 10 m) some diatoms occurred, such as *Tabellaria flocculosa, T. quadriseptata, Synedra vaucheriae* and *Aulacoseira distans v. alpigena*, which probably originated from the spring complex of phytoplankton.

Poverity of plankton flora was accompanied by dominance of the richly developed Zygnemales at the bottom and in the littoral zones. In the moss periphyton at the bottom *Zygnema* also dominated. In the littoral zone, where the substratum was formed by other higher plants, stones and dead wood, coenosis were constituted of *Zygnema, Mougeotia, Oedogonium* and *Hapalosiphon*. Red alga *Batrachospermum* was found at the edge of the swamp. Among the filaments there were a lot of benthic diatoms, such as *Tabellaria, Frustulia, Eunotia, Brachysira* (*Anomoeoneis*) and desmidiales, eg. *Cosmarium, Euastrum, Netrium*. Other groups of algae in Lake Chjuchyarvi and Lake Golubaya Lamba in summer were very poorly presented (Tables 1 and 2).

2.3 Lake Lishmenskoye and Lake Uros

In Lake Lishmenskoye and Lake Uros phytoplankton biomass ranged from 0.5 to 2.0 mg l^{-1}. *Synedra vaucheriae* and *Gonyostomum semen* in Lake Lishmenskoye and *Tabellaria quadriseptata* in Lake Uros were abundant but not clearly dominating. The biocoenosis was formed mostly by species belonging to Cyanophyta, Chlorophyta and Cryptophyta and also by *Dinobryon* and *Ceratium* species (Table 1). As compared with Lake Golubaya Lamba and Lake Chjuchyarvi, periphyton was more weakly developed. The filaments of *Zygnema* sp. and *Mougeotia* sp. were observed at the bottom and on the higher plants at the visible depth up to 3 – 4 meters. In the littoral zone the periphyton biocoenosis was formed by species of *Zygnema, Oedogonium, Bulbochaete, Mougeotia* and *Hapalopsiphon*. One of the dominant species, *Merismopedia glauca*, occurred in high densities in periphyton in Lake Uros. The species composition of the periphyton of these two lakes was quite wide and nearly all kinds of algae were present (Table 2). The littoral phytobenthos was dominated by filamentous green algae and diatoms.

3 DISCUSSION

There are no literature references available for the phytoplankton and the periphyton of Lake Golubaya Lamba, Lake Uros, Lake Lishmenskoye and Lake Chjuchyarvi. Taking into consideration the restriction of the data, it must be noted, that the present data gives only a general representation of the character and algal flora of these lakes. The number of taxa found in Lake Golubaya lamba (32) was much less than in Lake Chjuchyarvi. It can be explained, first, by the difference in size and depth, and second, by the absence of stratification in Lake Golubaya Lamba. The pH–indices were the same, 5.0 and 5.1, respectively.

Table 1. The most abundant species of phytoplankton in the studied lakes, (+ = abundant species, ++ = dominant species).

Species	Lake Golubaya Lamba	Lake Chjuch-yarvi	Lake Lishmen-skoye	Lake Uros
	pH = 5.0	pH = 5.1	pH = 6.4	pH = 6.5
CYANOPHYTA				
Anabaena lemmermannii P. Richt	–	–	–	++
Gloeocapsa minuta (Kuetz.) Holl.	–	–	–	+
Merismopedia tenuissima Lemm.	–	–	+	++
Merismopedia punctata Meyen	–	–	–	+
Merismopedia glauca (Ehr.) Naeg.	–	–	–	+
CRYPTOPHYTA				
Cryptomonas sp. cf. Marssonii Skuja	–	–	+	+
DINOPHYTA				
Ceratium hirundinella (O.F.M.) Bergh	–	–	+	–
Gymnodinium sp.	+	++	+	+
Peridinium inconspicuum Lemm.	++	++	+	+
CHRYSOPHYTA				
Chrysophyceae				
Chromulina microplancton Pasch	–	–	–	++
Dinobryon acuminatum Ruttn.	–	+	–	+
D. cylindricum v.palustre Lemm.	++	–	+	–
D. divergens Imh.	–	–	+	–
D. elegans Korsch.	–	+	–	–
D. pediforme (Lemm.) Steineke	+	–	–	–
Diatomophyceae				
Aulacoseira ambigua (Grun.) O. Muell	–	–	+	–
A. distans v. alpigena Grun.	–	+	–	–
Synedra vaucheriae Kuetz.	–	–	++	–
Tabellaria quadriseptata Knudson	+	+	+	++
T. flocculosa (Roth) Kuetz.	–	–	+	+
Raphidophyceae				
Gonyostomum semen (Ehr.) Diesing	–	–	++	–
CHLOROPHYTA				
Elakatothrix lacustris Korsch.	–	–	–	++
Sphaerocystris schroeteri Lemm.	–	–	–	+

In spite of the fact that the results of this study coincide with the data of other investigators (eg. Kippo–Edlund and Heitto 1990), who also found an average of 20 – 30 taxa in small forest lakes in Finland, it is possible that in connection with the small lake size that the plankton community has changed several times during the vegetative season. The total number of algal taxa in a small lake must be much more than observed during one summer survey. Nevertheless, one of the most characteristic species for acidic lakes, large and small, is *Peridinium inconspicuum* (Kippo–Edlund and Heitto 1990). It occurs all year around and can be a reliable indicator of acidic water, reaching complete domination in plankton. *Dinobryon pediforme* and *D. cylindricum*, as indicators, seems to be less reliable because their populations are not stable during the summer season.

Table 2. The most abundant species of algae in periphyton of studied lakes, (+ = abundant species, ++ = dominant species).

Species	Lake Golubaya Lamba	Lake Chjuch-yarvi	Lake Lishmen-skoye	Lake Uros
	pH = 5.0	pH = 5.1	pH = 6.4	pH = 6.5
CYANOPHYTA				
Hapalosiphon fontinalis (Ag.) Born. emed. Elenk	+	++	+	+
Stigonema sp.	–	+	–	–
Merismopedia glauca (Ehr.) Naeg	–	–	–	+
CHROMOPHYTA				
Diatomophyceae				
Achnathes minutissima v. *cryptocephala* Grun.	–	+	–	–
Anomeoneis serians v. *brachysira* (Breb) Hust.	–	+	–	+
Eunotia spp.	+	+	+	+
Fragilaria construens (Ehr.) Hust	+	–	–	–
Frustulia rhomboides v. *saxonica* (Rabenh.) D.T.	+	+	–	–
Pinnularia spp.	–	–	+	–
Tabellaria binales forma	–	++	–	–
T. flocculosa (Roth) Kuetz.	+	+	++	+
T. quadriseptata Knudson	–	+	+	+
Tribophyceae				
Tribonema sp.	+	+	–	–
CHLOROPHYTA				
Bulbochaeta sp.	?	+	+	–
Mougeotia spp.	++	+	+	+
Oedogonium spp.	+	+	+	+
Zygnema sp.	+	++	+	+
RHODOPHYTA				
Bathrachospermum sp.	–	++	–	++

In Lake Lishmenskoye and Lake Uros, *Peridinium inconspicuum* was not completely dominant during the investigation. The whole number of phytoplankton taxa in these lakes (pH was 6.4 and 6.5) was more than 100, typical of clearwater lakes of their mean size. The abundance of Cryptophyta and Cyanophyta in these weakly acidic lakes and their absence in Lake Golubaya Lamba and Lake Chjuchyarvi confirm the data of Finnish investigators (Kippo–Edlund and Heitto 1990).

Under highly transparent conditions phytoplankton occurred almost in the entire water column of the lakes studied. In the two acidic lakes, Lake Golubaya Lamba and Lake Chjuchyarvi, the algal community contained Zygnemales during the summer, which were spread over the whole bottom covered by water mosses and sphagnum. Sheltered by Zygnemales, several diatoms and probably some desmidiales were growing. Epilithic algae growing on bare stones in Lake Chjuchyarvi, were only slightly influenced by Zygnemales and reflected to a great degree the condition of the acidic water environment. They were not observed in the littoral zone of Lake Golubaya Lamba. Among these algae the most charasteristic taxon was *Tabellaria binalis*

(Lange–Bertalot 1988), which occurred in high densities only in Lake Chjuchyarvi. The most abundant diatom was *Tabellaria flocculosa*. The acidobiontic character of *Tabellaria binalis* is confirmed by the data of Finnish investigators (Huttunen and Turkia 1990). In the weakly acidic lakes the periphyton was composed approximately of mainly Zygnemales and other filamentous algae. The diversity of non–filamentous forms was much higher in this study (Table 2), however because of the low density they apparently do not contribute much to the primary production of the ecosystem.

In conclusion, Finnish observations showing the regularity of the decrease in species diversity from weakly acidic to acidic lakes is confirmed by this study. It is reflected not only by the phytoplankton and diatom flora but also by the periphytic algae. In acidic clear–water lakes, the production of periphytic algae and microphytobenthos may be significant by producing organic matter and thus supporting a high density of zooplankton populations. At the same time, these algae are one source of the supplement of phytoplankton during the vegetative season. The diatom *Tabellaria binalis* (Ehrenb.) Grun. found in Lake Chjuchyarvi, is a rare species, and requires a detailed study of its ecology and morphology.

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MACROPHYTES IN BIOMONITORING FRESH WATER ACIDIFICATION

Freindling A.V.

Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute

185003 Petrozavodsk
Urickogo 50
Russia, Republic of Karelia

1 INTRODUCTION

Acid rain is a wide–spread phenomenon in our time. It leads to essential acidification of the environment and to noticeable ecological modifications of whole regions, often at a long way from the source of the emission. The acidification of surface waters is one of the consequences of the progressive acidification of atmospheric precipitation. This phenomenon intensively takes place in North America and in some European countries – Finland, Sweden and Norway (Jeffries et al. 1986, Swedish Environmental Protection Board 1986, Henriksen et al. 1988, Landers et al. 1988, Forsius et al. 1990).

Areas sensitive for lake water acidification are also present in Russia, particularly, in the Murmansk region, Karelia and Siberia (Izrael et al. 1983). The most critical situation is in Karelia (Abakumov et al. 1986). The following are some of the causes for this problem:

1) A weak buffering ability of granites and gneises which are part of the rock structure in the watershed and form the bottom of numerous lakes,
2) wide spread sandy soils, the supeses which are the basis of the podzol soil formation with the acidic reaction of the environment and considerable accumulation of humus (Sokolov 1949),
3) the waterlogging of the territories, mainly the atmospheric and the swampy supplement of the water systems,
4) the low mineralization of the surface waters with low calcium and magnesium concentrations, and often high humus concentrations.

All these together with the predominance of acid sensitive territories in Karelia, and with the supposed increase of the acidification of the atmospheric precipitation (up to pH 3.5 – 4.0), inevitably leads to the acidification of Karelian lakes.

The negative ecological consequences of acid rain are displaced in gradual degradation of the ecosystems of water bodies – in particular, in the simplification of the phytocenosis structure, in the decrease of the floral diversity and in the reduced intensity of the production processes.

2 MACROPHYTES AND ACIDIFICATION

Macrophytes are visible to the naked eye, making them highly convenient objects for observations. They give the opportunity in a biological survey of the water body to initially estimate by sight its ecological state. They allow the determination of the trophic properties of water and also sometimes its chemical specificity (Abakumov 1977), especially in reference to the bioindex of clean waters.

Under the definition of bioindex, certain plant species serve as important indicators. However, there are some difficulties using such plants because many of them have a wide ecological and geographical range. Moreover, in different physico-geographical conditions plant indicators can occur in water bodies of different trophic states, and accordingly, they can serve different indicator significance. The restriction of the information concerning the ecology and the physiology of such plants, which serve as indicators, is the limiting factor (Katanskaya and Raspopov 1983). However, higher aquatic plants can be successfully used as indicator plants of the water bodies and the water courses acidification.

As the pH in lake water decreases, the number of macrophyte species decreases and the abundance and frequence of macrophytes decreases. Most macrophytes cannot survive in very acidic water. Chernov (1949) observed that in the lakes where pH was lower than 6.8, the first macrophytes to disappear were the species of Potamogetonaceae, which usually are common in the littoral zone of Karelian lakes. The last to disappear was *Potamogeton natans*, then Holarrhagitaceae. In acidic lakes stands of *Phragmites* sp. and *Equisetum* sp. were sparse. This phenomenon was noticed in the study of dystrophic lakes of the River Shuja basin (Chernov 1949).

Sphagnum mosses prefer acidic water (pH less than 6) and thrive in the lakes that have become acidic. The abundance of *Sphagnum cuspidatum* has increased along with lake water acidification in Sweden (Grahn 1976) and in North America (Hendrey et al. 1980). Moreover, abundant *Sphagnum cuspidatum* stands outcompeted *Lobelia dortmanna* areas. *Sphagnum* mosses can also increase the acidity because of their high ion-exchange capability (Grahn et al. 1974, Hendrey and Vertucci 1980).

Species of *Nymphaea* are more stable against acidification since they take nutrients from sediment where the pH is higher (Hultberg and Grahn 1975). It is necessary to take into consideration that many plant species can grow in acidic waters for some time before showing effects of acidification.

3 MACROPHYTES IN ACIDOTROPHIC LAKES IN KARELIA

There are more than 61 000 lakes in Karelia (see Gasheva 1967). They can be divided into acidotrophic, dystrophic, oligotrophic, mesotrophic and eutrophic. In recent years, in connection with the acidification by anthropogenic factors, the tendency of further acidification of some lakes is clearly seen.

The nature of acidotrophic lakes is rather unique. Zernov (1934), while characterizing acidotrophic lakes (pH < 5.5), noted that they may have both colourless and brown coloured water. The second case takes place by the combination of acidotrophy and dystrophy. By terminology of Baranov (1958), the first group of lakes ought to be called acidotrophic–oligotrophic oligohumic, the second acidotrophic–dystrophic polyhumic.

3.1 Acidotrophic–oligotrophic oligohumic lakes

As a rule, acidotrophic–oligotrophic oligohumic waters are small with a small catchment area. *Sphagnum* mosses are quite common near the shoreline, but the proportion of peatlands in the catchment area is small. The dominant soil type is silt with some undecomposed moss.

By the work of Kharkevich (1970), to acidotrophic–oligotrophic oligohumic waters can be included the following lakes in Karelia: Livozero, Stolpozero, Svetloe, Bachanskoe, Aglimozero (the east shore of Lake Onega) and also lakes Uros and Golubaya Lamba (on the basin of River Suna).

Macrophytes typical for oligotrophic, clear–water lakes, such as *Lobelia dortmanna* L., and *Myriophyllum alterniflorum* D.C., are common also in acidotrophic–oligotrophic oligohumic lakes. The frequence and the biomass of macrophytes in these lakes are low.

In Lake Aglimozero only 2 % and in Lake Stolpozero only 6 % of the lake area was covered by macrophytes (Kluykina 1970). In these lakes macrophytes covered 21 % to 69 % of the lake shoreline. Dominant macrophytes were floating leaved species. The number of species ranged from 4 (Lake Aglimozero) to 15 (Lake Livozero).

In Lake Uros 2.1 % of the lake area was covered by macrophytes, with the plant region of the lake approaching 50 % (Freindling 1981). The most significant were the air–aquatic plants; the dominant was *Nuphar–Nymphaea* cenosis. The number of species was 22.

3.2 Acidotrophic–dystrophic polyhumic lakes

Acidotrophic–dystrophic polyhumic waters vary by the lake area, often they are considerably large with comparatively large cathment areas. The proportion of peatlands in the catchment area is usually high, 20 – 50 %. The upper and the transitional swamps dominate. The lakes, as a rule, are not deep. The typical representatives of this group are lakes Vegarusjarvi, Salonjarvi (on the basin of River Shuja) and Hizozero (Kharkevich 1970).

Acidotrophic–dystrophic polyhumic waters are determined by the predominance of helophytes such as *Carex* sp. *Menyanthes trifoliata* L., *Comarum palustre* L., *Naumburgia thyrsiflora* (L.) Renb. *Hippuris vulgaris* L. and *Utricularia vulgaris* L. are also quite common. Small amounts of *Myriophyllum alterniflorum* D.C. and *Lobelia dortmanna* L. are also found. The acidic reaction of the environment and the low water transparency limit the spreading of elodeids.

By the work of Freindling (1981), the overgrowth level of acidotrophic–dystrophic polyhumic lakes was not large, 2.4 % in Lake Salonjarvi, and 2.2 % in Lake Vegarusjarvi, the proportion of shoreline cover ranging from 17 % (Lake Salonjarvi) to 40 % (Lake Vegarusjarvi). The number of species comprised of 14 and 17 species, respectively. The dominant species in Lake Vegarusjarvi were *Carex* spp. and *Phragmites–Equisetum* cenosis. In Lake Salonjarvi side by side with *Carex* sp. were also *Menyanthes trifoliata*, *Naumburgia thyrsiflora* and *Sparganium affine* Schnirl.

4 MACROPHYTE MONITORING PROGRAMME FOR AIRBORNE ACIDIFICATION IN KARELIA

In order to monitor the acidification process in the surface waters of Karelia, different lakes has been chosen from different parts of Karelia. These are lakes Vendurskoe and Golubaya Lamba (the River Suna basin), Lake Urozero (the River Shuja basin), Lake Tubozero (the eastern Prionezje), and Lake Ladmozero (Zaonezski peninsula) in southern Karelia, and Lake Kamennoe in northern Karelia. The lakes have different hydrochemical properties, e.g. wide pH range. Differences in macrophyte communities will be studied.

Higher aquatic plants are undoubtedly more conservative indices of water quality in comparison to other parts of the ecosystem; they are more stable to lake water acidification. Changes in the degree and character of overgrowth in the water body, floral composition, development of biomass and production of the macrophytes, including their chemical composition, can mark the acidification process in natural waters. These transformations of water ecosystems require greater attention.

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ACIDIFICATION AND TRACE METALS IN LAKES

Jaakko Mannio

National Board of Waters and the Environment
Water and Environment Research Institute
P.O.Box 250
FIN-00101 Helsinki, Finland

1 INTRODUCTION

Headwater lakes receive atmospheric trace metals directly from precipitation, dry fallout and snowmelt. The inflow is also dependent on the complex weathering, leaching and retention reactions that occur in the catchment area. Many trace metals are emitted, as well as deposited, together with acidic compounds and acidification of soils can increase the leaching of some metals and change the sedimentation processes in the lakes (e.g. Bergqvist 1987, Dillon et al. 1988, Norton & Kahl 1991). The objective of this paper is to present the main results of a survey of trace metal concentrations in the water of small headwater lakes and discuss their relations to deposition and environmental conditions, in particular, acidity, organic carbon and catchment characteristics including till geochemistry. A more detailed description of the material and methodology, as well as part of the results, have been previously presented (Verta et al. 1990).

2 MATERIAL AND METHODS

The lakes for trace metal sampling were selected subjectively from the 1189 survey lakes of The Finnish Acidification Research Programme in 1987 (Forsius et al. 1990). The lakes were situated in sparsely populated areas at the head of a drainage basin. Some of the southernmost lakes were, however, only some 20 km from the nearest municipalities. The lakes normally occupied about 10 – 20 percent of the watershed. Mean area of the lakes was 0.38 km^2; the largest was 10 km^2.

The lakes were chosen to represent the lake population of Finland but are concentrated in areas which have the highest deposition of acidic compounds. About half of the lakes were also sites of intensive research concerned with the effects of acidification on the biota of lakes (Eloranta 1990, Heitto 1990, Huttunen et al. 1990, Huttunen & Turkia 1990, Kippo-Edlund & Heitto 1990, Meriläinen & Hynynen 1990, Rask & Tuunainen 1990, Sarvala & Halsinaho 1990). The watersheds were primarily coniferous forests or peatlands, till being the most common soil material. Ditching operations are the main disturbance in most watersheds. Cultivated land was normally absent and in no case exceeded ten percent of the watershed area.

Heavy metal samples of lake waters were taken below the surface layer directly into 125 ml polypropylene bottles (Nalgene labware) following a recent Finnish standard (SFS 5503) to prevent contamination. Graphite furnace AAS was used for the determination of Cd, Cu, Pb and Ni and flame AAS for Zn. Iron and Mn were determined colorimetrically according to Finnish standards (SFS 3028, SFS 3033) and total monomeric Al according to Røgeberg and Henriksen (1985).

Mapped data of metal concentration (Cd, Cu, Pb, Zn and Ni) in moss (Ruhling et al. 1987) were used as an indirect estimate of metal deposition in different regions. Concentration of metal (Cu, Zn, Ni, Mn, Fe and Al) in till fine fraction (< 0.06 mm, partial dissolution in aqua regia) (Koljonen 1992) was used to depict the potential influence of soil material on metal concentrations in lake waters. One value for each metal was interpolated from the original till dataset for each individual lake.

Statistical evaluations (SAS software) included the examination of the distributions of the parameters, transformation to a logarithmic scale to enhance the normality, correlation analysis between the variables to identify the strength of the relationships and to reveal colinearity in the final analysis, and the stepwise multiple regression analysis.

3 RESULTS AND DISCUSSION

The general water quality of the studied lakes was close to the average of small Finnish lakes (Forsius et al. 1990). Acid-sensitive, dilute clearwater lakes were somewhat over-represented in the lakes studied here, resulting in slightly lower median values of conductivity, pH, alkalinity and total organic carbon (Table 1).

Table 1. General characteristics of the lakes (n = 256).

	Unit	Percentiles		
		10 %	Median	90 %
Lake area	km^2	0,03	0,15	0,80
Watershed area	km^2	0,30	1,35	7,50
Peatlands	%	3	13	41
Exposed bedrock	%	0	0,5	21
Conductivity	$mS\ m^{-1}$	1,4	2,6	4,3
pH		4,9	6,0	6,9
Gran alkalinity	$\mu eq\ l^{-1}$	-20	32	140
SO_4*	$\mu eq\ l^{-1}$	30	73	150
Base cations*	$\mu eq\ l^{-1}$	82	190	330
TOC	$mg\ l^{-1}$	2,3	7,2	19
Total P	$\mu g\ l^{-1}$	5	10	26

* sea-salt corrected values

The order of concentration of the trace metals was: Fe > Al > Mn > Zn > Cu-Ni > Pb > Cd (Table 2), the same order and comparable average concentration as in similar Swedish lakes (Borg 1983, 1987), but lower than in those from the southern Norwegian survey in 1974-75 (Table 3).

Table 2. Trace metal concentration (µg l^{-1}) in Finnish lakes. The lower number of lakes for Cd, Pb and Zn is due to rejections of some areas with high reagent blanks.

	Percentiles			
	10 %	Median	90 %	n
Cd	< 0.01	0.02	0.06	(190)
Pb	< 0.01	0.08	0.25	(172)
Ni	< 0.10	0.19	0.66	(242)
Cu	0.11	0.32	0.77	(242)
Zn	< 1.0	2.7	7.2	(171)
Mn	5	23	64	(253)
Al	< 10	38	150	(256)
Fe	27	190	910	(254)

Table 3. Mean values of trace metal concentrations in water (µg l^{-1}) in Scandinavian surveys of small headwater lakes.

Region	Cd	Pb	Cu	Ni	Zn
South Finland[a]	0.03	0.13	0.38	0.40	5.6
C.+N. Finland[a]	0.02	0.12	0.43	0.25	2.5
South Sweden[b]	0.04	0.67	0.68	< 1.0	11.0
C.+N. Sweden[c]	0.014	0.27	0.51	0.42	2.2
South Norway[d]	0.2	2	2	..	15

[a] Verta et al. 1990
[b] Borg 1983
[c] Borg 1987
[d] Henriksen and Wright 1978 (median values)

Lead and to some extent Cd and Zn values in the present study are lower than in Sweden and in a preliminary study in Finland (Mannio and Verta 1987). The latter sampling occurred in May after snowmelt, a period which probably represents the higher concentrations of the year for anthropogenic metals. Autumn values could merely be compared to summer values, when high production and input of particulate matter increases the sedimentation and hence lower the concentration in water (White and Driscoll 1985). Borg (1987) found on average 3.1 times lower Pb and 2.4 times lower Cd concentration in summer than in winter.

The concentrations of Zn, Ni and Cd in water decreased northward, parallel to the pattern of atmospheric deposition according to snowpack chemistry. Also the soil derived metals, Mn and Al, clearly decreased towards the north (Verta et al. 1990).

Comparison of lake water chemistry data with metal concentration in moss (Ruhling et al. 1987) revealed that Cd, Cu, Pb, Zn and Ni all had higher average concentrations in water, the higher was the regional concentration of the same metal in moss (Verta et al. 1990).

It is difficult to determine the influence of acidification from the increased atmospheric loading of (heavy) metals without detailed catchment studies (e.g. Nelson and Campbell 1991). An attempt was made to minimize the regional differences in metal loading by grouping the lakes according to mapped moss metal concentration to "standardized" deposition classes of each metal (Table 4). We also rejected smaller areas primarily in southwestern and northeastern Finland with high metal deposition from local sources. This grouping suggested, that acidity and/or acidification is the primary factor determining the lake metal concentration. For Zn, Cd and Pb the pH value explains much of the variation, while other factors (percent of exposed bedrock on the catchment and SO_4* for Zn, lake area for Cd and Pb and TOC for Pb, all in a positive direction) explain only 4 to 9 percent of the variation (Table 4).

Table 4. Significant correlation coefficients between metals in water (log transformed) and environmental variables (log transformed except non-marine SO_4*). Area refers to regional metal concentration in the moss survey (s = South Finland, c = Central Finland etc.) (Ruhling et al. 1987). Till refers to the concentration of the same metal in till fine fraction (see text). R^2 is percent explained from the total variation of the metal concentration by stepwise regression analysis including 2 to 4 independent variables (F-statistics $P < 0.01$).

	n	Area	pH	SO_4*	TOC	Till	R^2
Zn	108	c+e+n	-0.521***	0.210*	0.238*	0.227*	35
	63	s+w	-0.651***	-	-	-	50
Cd	134	s+w+c	-0.381***	-	-	..	21
	48	e	-0.625***	-	-	..	39
Pb	99	c	-0.454***	-0.310**	0.224*	..	27
	57	s	-0.627***	-	0.331*	..	48
Ni	149	c+n	-0.271***	0.427***	0.291***	0.239**	33
Cu	196	s+c+n	-	-	0.358***	0.319***	20
Mn	253	all	-0.405***	0.321***	0.402***	0.129*	35
Al	256	all	-0.685***	0.253***	0.534***	-	69
Fe	254	all	-0.267***	-	0.833***	-	72

*** = $P < 0.001$
** = $P < 0.01$
* = $P < 0.05$
– = not significant
.. = no data

The terrestrial input of dissolved humic substances from the catchment is an important carrier of metals to small lakes located in forested areas (e.g. Borg and Johansson 1989). The concentration of the mainly land derived metals, Al, Fe, and Mn, are strongly dependent on total organic carbon (TOC), as well as on acidity. The concentrations of Cu and Ni in lake waters are more strongly dependent on TOC than those of Cd, Zn and Pb.

These relationships between metals, pH and TOC are similar to, but more significant, than those reported in previous survey studies in Sweden (Borg 1983, 1987) and Finland (Mannio and Verta 1987), due to much larger material in the present study.

The concentration of Cu, Ni and to some extent Mn and Zn in till material is correlated to the concentration of the same metal in lake waters. However, in the stepwise regression analysis, only the explained variation of Cu in water is significantly ($P < 0.01$) enhanced by introducing the Cu concentration in till into the equation. Also other catchment characteristics, such as peatlands, exposed bedrock, catchment: lake area –ratio are correlated to metal concentrations, but the colinearity with water quality parameters (pH and organic carbon mostly) is usually so strong, that the degree of explanation of the models does not improve.

The results of this survey are consistent with the observations of intensive catchment mass balance and lysimeter studies. The concentration of metals in small lakes in forested areas depends on environmental conditions, including atmospheric deposition of both metals and acidic compounds. These conditions are quite well reflected by a few, integrating water quality variables.

4 SUMMARY

Concentrations of metals (Cd, Pb, Ni, Cu, Zn, Mn, Al and Fe) were measured in 256 lakes as a part of a national acidification survey in the year 1987. Concentrations generally followed the pattern of atmospheric deposition according to snowpack and moss chemistry. When the lakes were grouped by metal concentration in moss, lakewater acidity (except for Cu) and the concentration of organic carbon (except for Cd) were most significantly correlated to metal concentrations in lakes. In a stepwise regression analysis, these two variables together with a few catchment characteristics accounted for about 70 percent of the variation of Fe and Al, and 20 to 50 percent of the variation of the other metals. Copper concentrations in lakes were significantly explained by the regional Cu concentration in the fine fraction of till.

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EXPERIMENTAL RESEARCH ON HEAVY METAL TOXICITY IN AN ACIDIC ENVIRONMENT

Dubrovina L.V., Fedorova N.V. and Pomazovskaja I.V.
Karelian Research Center
Russian Academy of Sciences
Northern Water Problems Institute

185003 Petrozavodsk
Urickogo 50
Russia, Republic of Karelia

1 INTRODUCTION

Acidification is a serious problem for aquatic ecosystems because of its many influencing factors. pH is the most significant ecological factor exerting a nonspecific influence on the degree of toxicity of different substances and also on the level of the resistance of the organisms. Therefore when studying the processes of acidification it is necessary to consider both the direct and indirect influence of pH. The direct approach involves determining the effects of hydrogen ions on the physiological functions of organisms. Indirect study involves monitoring the change in the toxicity level of substances at the expense of different transformations, which are determined by changes in the pH level.

The variety of metal migration forms in fresh waters is determined by their different chemical properties and by the influence of biotic and abiotic environmental factors. Under acidification the most essential changes are associated with the increase of metal ion forms (MgKnight 1981, Linnic and Nabivanez 1988, Vinogradov et al. 1988, Mur and Ramamuri 1987).

The biological activity of different metals varies, hence effecting aquatic organisms in various ways. The most toxic metals are those which have non-complexed ions.

In this study the toxicity of heavy metals, copper and nickel, in an acidic environment is investigated. The more toxic of the two metals studied is copper. Hydrogen ions influence the absorption of copper by hydrobionts in many ways. At low levels of pH, the number of free ions increase, with copper toxicity being higher in acidic water than in alkaline water. The absence of complex-formation remains (ligands) in water promotes an increase in metal toxicity (Linnic and Nabivanez 1988, Mur and Ranamuri 1987). According to Linnic and Nabivanez (1988), in ionic form, nickel toxicity increases two fold. However, in an acidic environment, it usually binds to sulphate and fulvite complexes.

2 MATERIAL AND METHODS

The aim of this researcch is to study the influence of low pH levels on the toxicity progress of hydrobionts under the influence of copper and nickel salts in low mineral content waters. The experiments were carried out by generally accepted methods.

Aquatic invertebrates were studied using the water of Lake Vendurskoe (natural pH 6.5), with acidification up to pH 4.5 and pH 5.5 and using the water of Lake Golubaya Lamba (natural pH 5.03). Nickel concentrations were 0.5 mg l^{-1} and 1.0 mg l^{-1}. Invertebrates for the tests were taken from Lake Vendurskoe. The experiments were divided into four groups according to the type of water used to prepare the solutions, and the acid used for acidification (Table 1).

Toxicity was estimated using the following criteria:

- survival of test organisms
- hatchability dynamics
- linear-weight measures of larvae
- malformation phenomena
- behaviour reaction of invertebrates

The analyses of fatty acids of trout larvae (*Salmo irideus*, Gibbons) were made in the biochemical laboratory of Biological Institute in Karelian Research Center of Academy of Russia.

Table 1. Experimental scheme.

Variant	Initial water	pH	Acid	Test-organism	Test-reagent	Exposition (days)
I	City water chlorineless water Lake Onega	6.8	-	*Coregonus lavaretus* and *Salmo irideus* (Gibbons) spawn and larvae	$CuCl_2$	91 41
	Lake Onega	5.5	H_2SO_4	-"-	$CuCl_2$	41, 46
	Lake Onega	6.8	-	*Coregonus lavaretus*	$NiCl_2$	85
		5.5	H_2SO_4	spawn and larvae	$NiCl_2$	85
II	Lake Vendurskoe (mesotrophic, meso-humous type)	6.5 7.0	-	*Daphnia longispina, Diaphonosoma braphyurum, Eurycercus,*	$NiCl_2$	4
	-"-	5.5	H_2SO_4	*Acantocyclops nanus,*	-"-	-"-
	-"-	4.5	H_2SO_4	*Macrocyclops albidus, Asellus aquaticus, Limnephilus borealis, Oligochaeta*	-"-	-"-
III	Lake Golubaya Lamba (clear water oligotrophic type)	4.0	-	-"-	-"-	-"-
IV	City water chlorineless water Lake Onega	6.8	-	*Daphnia magna* (laboratory culture)	$NiCl_2$	4
	-"-	6.0	H_2SO_4	-"-	-"-	-"-
	-"-	6.0	HNO_3	-"-	-"-	-"-
	-"-	6.0	HCl	-"-	-"-	-"-
	-"-	6.8	-	*Coregonus lavaretus* and	-"-	10
	-"-	3.5	H_2SO_4	*Coregonus albula*		-"-
		-5.5	HNO_3	spawn and larvae	-"-	

3 RESULTS AND DISCUSSION

3.1 The influence of copper on *Coregonus lavaretus* and *Salmo irideus* (Gibbons) in the early ontogeny period

Studies showed that copper had a sharp lethal effect on *Coregonus lavaretus* spawn at a concentration of 0.5 mg l^{-1} and on *Salmo irideus* (Gibbons), the more sensitive test organism, at a concentration of 0.5 mg l^{-1} and 0.1 mg l^{-1} both in acidic and neutral conditions. The LT_{100}(0.5 mg l^{-1}) (= lethal time) of *Salmo irideus* (Gibbons) was 21 days under both conditions. During the experiment spawn were covered by a white thin coating, which was formed as a result of the reaction between metal and slime secretion.

Metal was the main constituent of solutions having high copper concentration. Under the influence of relatively large toxic doses, the regulation system of the organism cannot keep pace and it becomes suppressed. Therefore the processes under acidic conditions, in small doses, should be investigated.

The pH influence of copper toxicity was observed in the solutions with the following copper concentrations:

- 0.1, 0.05, 0.01, 0.005 mg/l (*Coregonus lavaretus*)
- 0.01, 0.005 mg/l (*Salmo irideus*, Gibbons)

In studies of *Salmo irideus* (Gibbons) spawn mortality was already high during the first days of the test. In the neutral environment the survival of embryos and larvae did not differ from the control (Fig. 1a and 2a). Obviously the negative effect of copper intensification was reflected in hatchability dynamics, since it is the pre--larval stage in the ontogeny of fish which is the most sensitive (Fig. 1b, 2b).

In an acidic environment the copper toxicity threshold decreased. The lethal concentration (LC_{50}) value, after a 40 day period for *Salmo irideus* (Gibbons) spawn, in unaltered water, ranged from 0.05 mg l^{-1} to 0.1 mg l^{-1} and in acidic water from 0.005 mg l^{-1} to 0.01 mg l^{-1}.

The analyses of fatty acids of *Salmo irideus* (Gibbons) larvae were made under the metal concentrations of 0.01 mg l^{-1} and 0.05 mg l^{-1}. The compositon of total lipids and phospholipids of *Salmo irideus* (Gibbons) larvae, developed in an acidic environment with copper, was essentially different from the control. The change of saturation of membrane lipids is assosiated with penetrability and disturbances of other properties, and correlates with high mortality and changes in larval development.

Coregonus lavaretus and *Salmo irideus* (Gibbons) spawn and larvae, developed in pH 5.5 without reagent, did not differ from the control (pH 6.9). Reagent influence was observed only in the change of larvae weight parameters.

According to this experiment, the early ontogeny period for fish is affected by copper toxicity intensification under acidic conditions. Evidently, this is connected with the increase of metal ion formations which are the most bioactive.

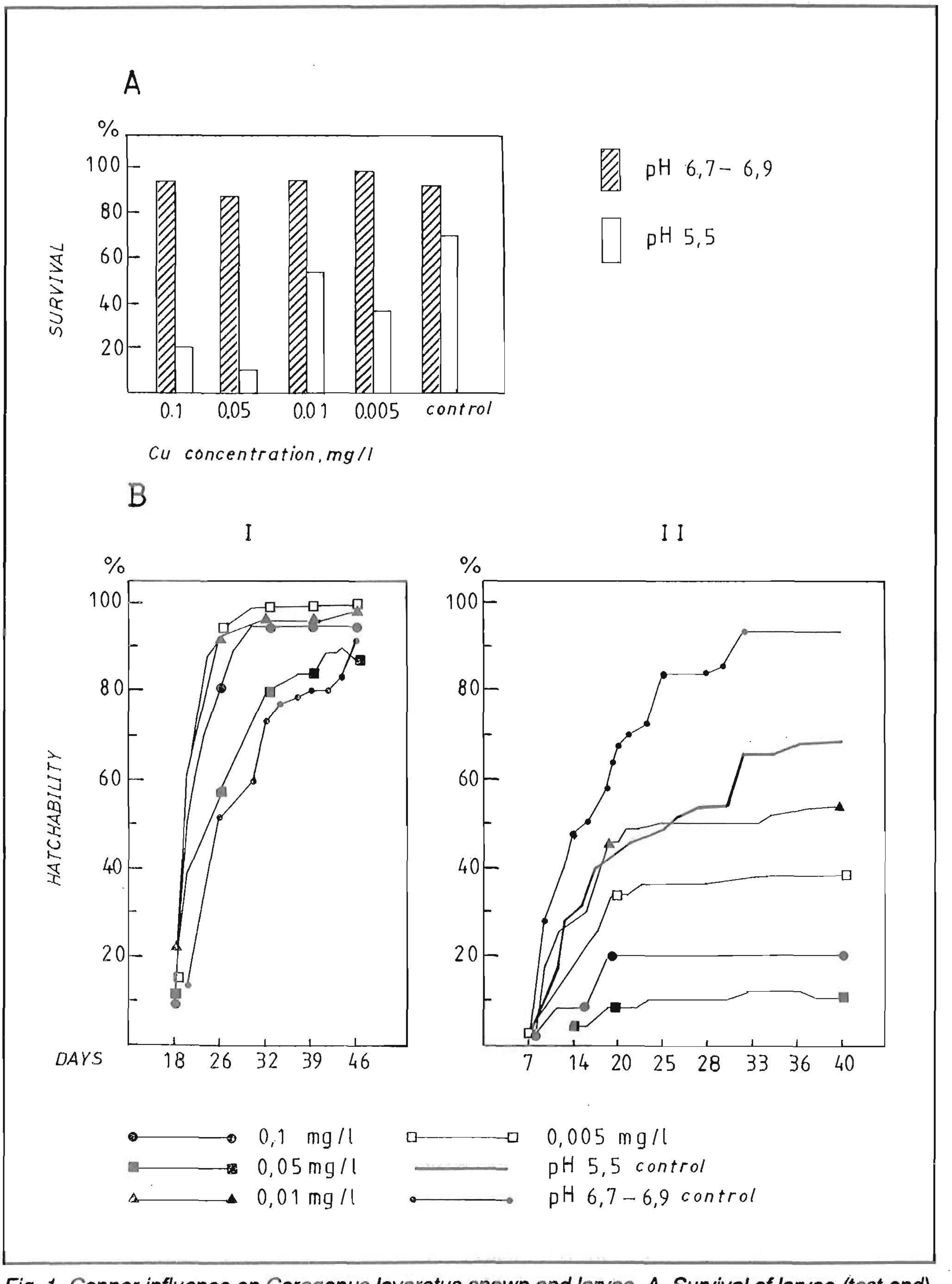

Fig. 1. Copper influence on Coregonus lavaretus spawn and larvae. A. Survival of larvae (test end), B. Hatchability dynamics of larvae (I. Test in pH 6.7-6.9; II. Test in pH 5.5)

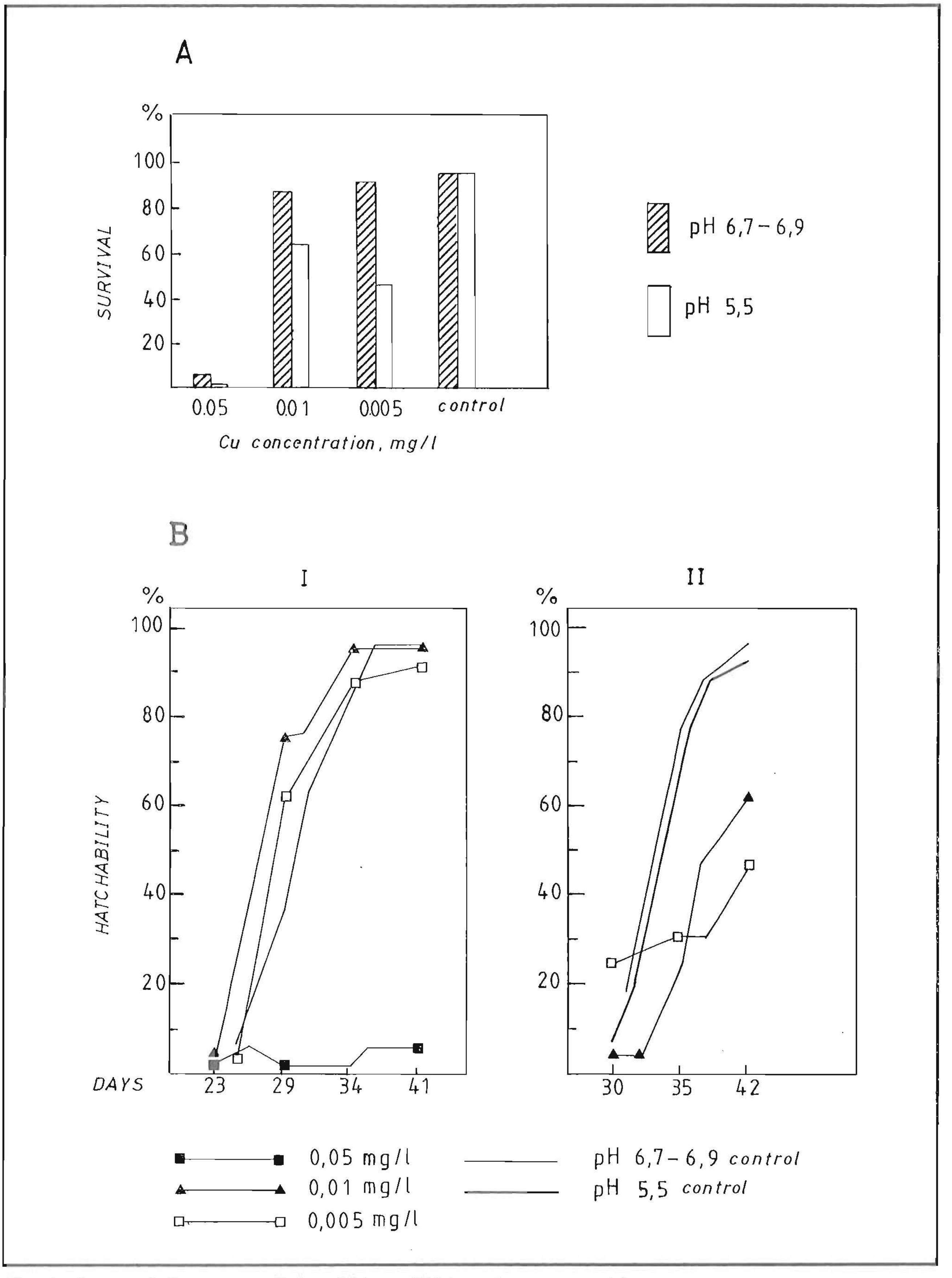

Fig. 2. Copper influence on Salmo irideus (Gibbons) spawn and larvae.
A. Survival (test end),
B. Hatchability dynamics of larvae (I. Test in pH 6.7–6.9; II. Test in pH 5.5)

3.2 The influence of nickel upon *Coregonus lavaretus* and *Coregonus albula* in the early ontogeny period and upon invertebrates

The study of nickel toxicity in an acidic environment, performed under the same conditions as for copper, did not clearly show an effect of pH. The toxicity is apparently closely connected with the form of nickel in water.

Initially (before the formation of red blood cells), nickel, in a range of studied concentrations (0.1, 0.05, 0.01 and 0.005 mg l^{-1}) did not exert an essential influence upon the survival of *Coregonus lavaretus* spawn, in either acidic or neutral waters. Over a 40 day period, the LC_{50} value at pH 5.5 was 0.010 mg l^{-1} and at pH 6.9 was 0.014 mg l^{-1}. The general number of spawn before hatching and the final number of larvae at the end of the test in unaltered and acidic environment at a nickel concentration of 0.01 mg l^{-1} and 0.005 mg l^{-1}, were quite similar. Moreover, the number of unhatched spawn in these test solutions was considerably low.

However, a considerable reduction in the survival of spawn and larvae occured in acidic waters with the highest concentrations of nickel (0.1 and 0.05 mg l^{-1}) over a 40 day period, at the membrane softening stage, when spawn are their most sensitive (Fig. 3a). After 40 days, there was a marked difference in the larvae linear–weight measures as compared to the control. Initially, changes were within the normal range. However after prolonged and constant exposure to Ni, the effects acquired a pathological character. This may be a functional phenomenon.

Hatchability dynamics were complicated (Fig. 3b). In the course of the experiment, in neutral and acidic conditions, there appeared malformed embryos that died before hatching. The malformation had a specific character.

The negative effects of metal on the embryo in the period of organogenesis caused some disturbance in the formation of the skeleton structure: the bifurcation of the head section and the mid–body section (the head is connected with the tail), the undeveloped body and the absence of a tail section (Fig. 4).

An examination of the effect of metal upon *Daphnia longispina* showed that the differences between survival curves at studied pH levels were not significant. The boundary between survival indices at pH 5.5 and pH 6.53 in the presence of nickel was not observed in any of the tested organisms. A small change in the dynamics of *Eurycercus* was noted (Fig. 5). At pH 4.4 there was an intensification of nickel toxicity at concentration of 1.0 mg l^{-1} only upon *Macrocyclops* and *Eurycercus*, which could be explained by the combined effect of Ni^{2+} and H^{+} ions.

As espected, hydrobionts with a narrow range of tolerance to environmental pH were highly sensitive to strongly acidic waters (*Diaphonoma braphyurum, Eurycercus sp., Limnophilus borealis*).

The effects of nickel toxicity on Oligochaeta was observed in water from Lake Golubaya Lamba. The different reaction of Oligochaeta to the presence of metal in water from Lake Vendurskoe and from Lake Golubaya Lamba testified that metal toxicity depended not only on the pH level of environment but also on the chemical composition of natural water. Experiments in this field will continue.

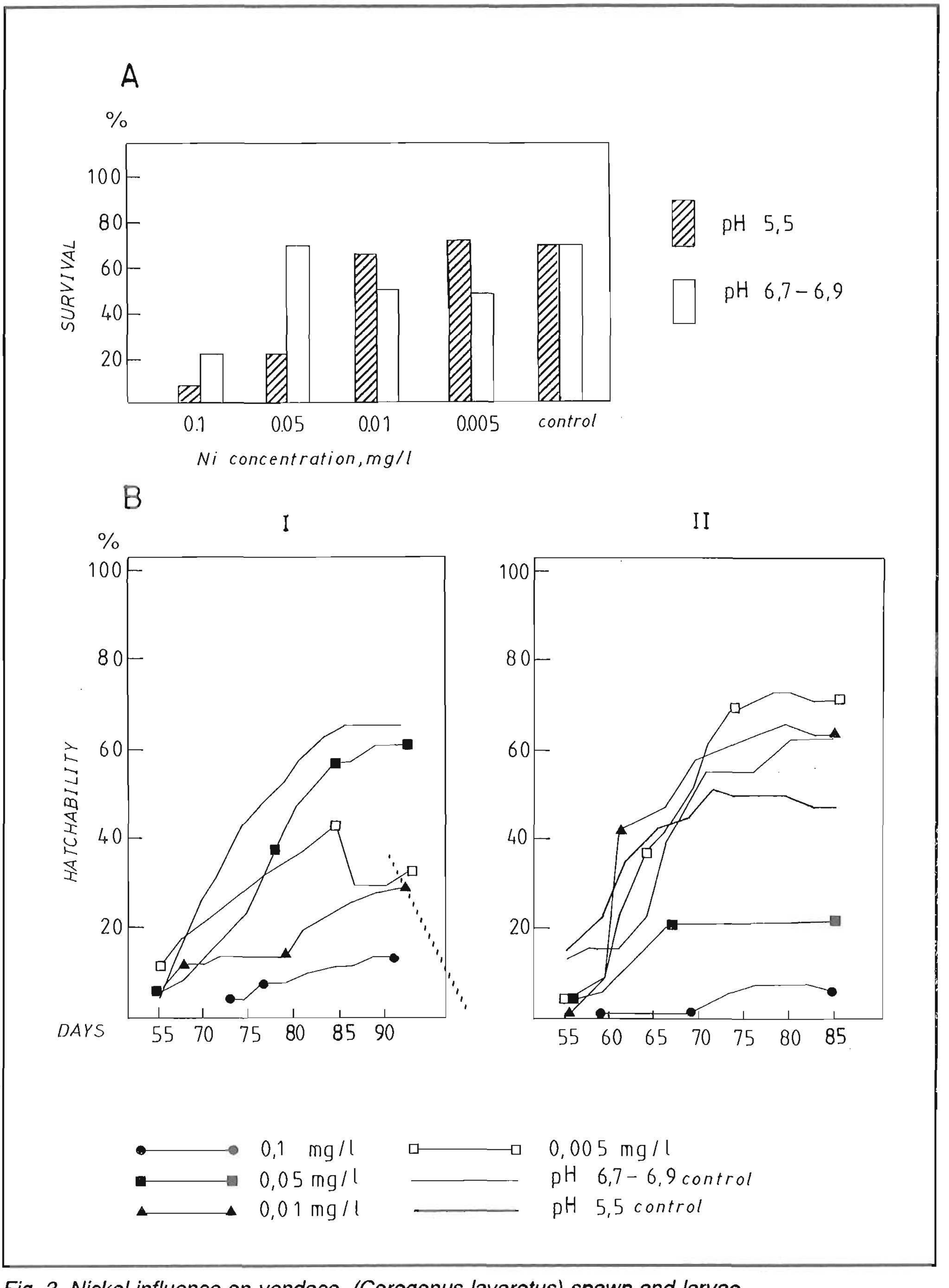

Fig. 3. Nickel influence on vendace, (Coregonus lavaretus) spawn and larvae.
A. Survival (test end),
B. Hatchability dynamics of larvae (I. Test in pH 6.7–6.9; II. Test in pH 5.5)

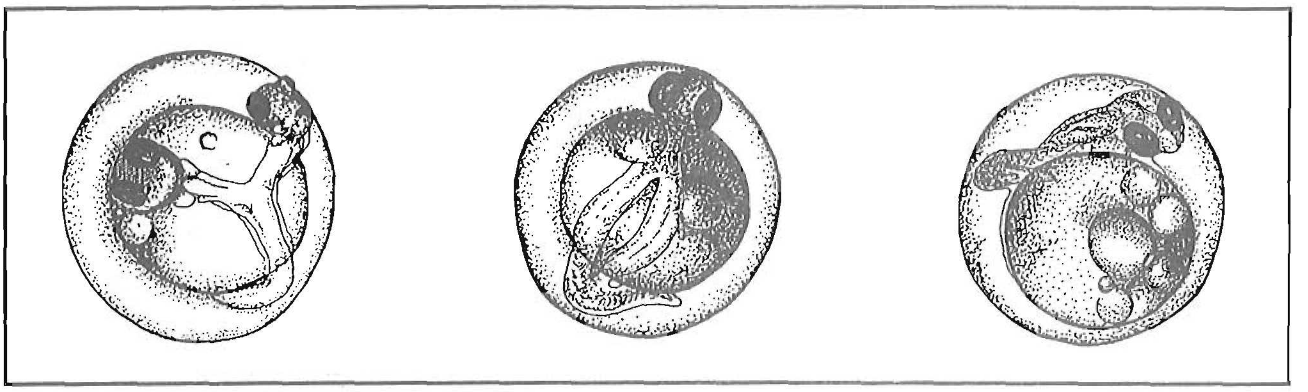

Fig. 4. Embryo malformation phenomenon in nickel solutions.

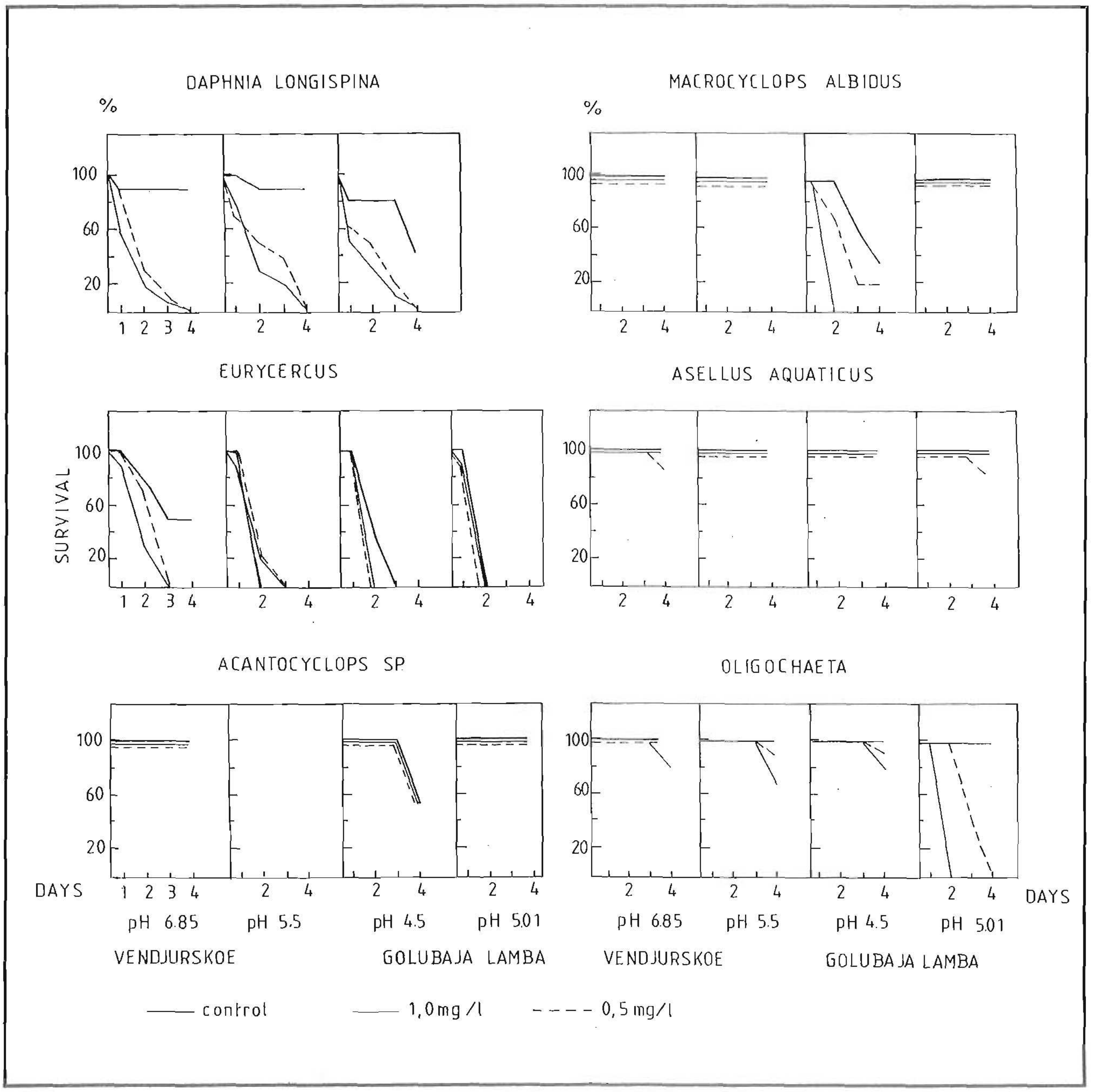

Fig. 5. Survival of test organisms in nickel chloride solutions at different pH levels.

Thus, according to these experiments, the clear dependence of nickel toxicity on the pH of the environment was absent. Naturally, one could propose that in this case metal activity was conditioned not so much by the concentraton of hydrogen ions, but by the combinations of complex-formations present in water which reduce the biological activity of nickel. Because the acidification of solutions were made by sulphuric acid, it was possible that there was an interaction between sulphate and nickel ions with the result of stable complexes. To confirm this hypothesis additional tests were made using different acids.

In nickel concentrations of 0.1 mg l^{-1}, with artificial lowering of pH to pH 6.0 by different acids (H_2SO_4, HNO_3, HCl), the survival of *Daphnia* varied (Fig. 6). A negative influence of nickel in acidic solutions using sulphate ions was not observed.

Also *Coregonus lavaretus* and *C. albula* spawn were exposed to artificially acidified conditions, pH 3.5, pH 4.0, pH 4.5, pH 5.0 and pH 5.5. The acidification agents were H_2SO_4 and HNO_3 (Fig. 7). During the experiment the tested spawn could withstand low pH levels, up to pH 4, for 10 days. Under these conditions the reactions of organisms depended on the presence of acid anions. The simultaneous presence of hydrogen and sulphate ions in water can relax the adverse effects of nickel.

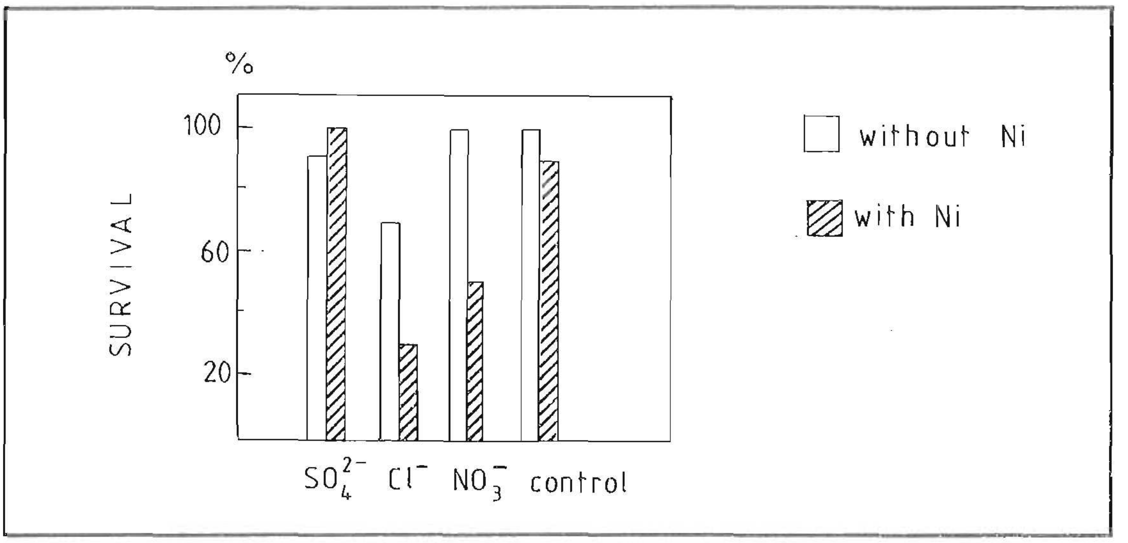

Fig. 6. Survival of Daphnia at the end of 4-d exposure.

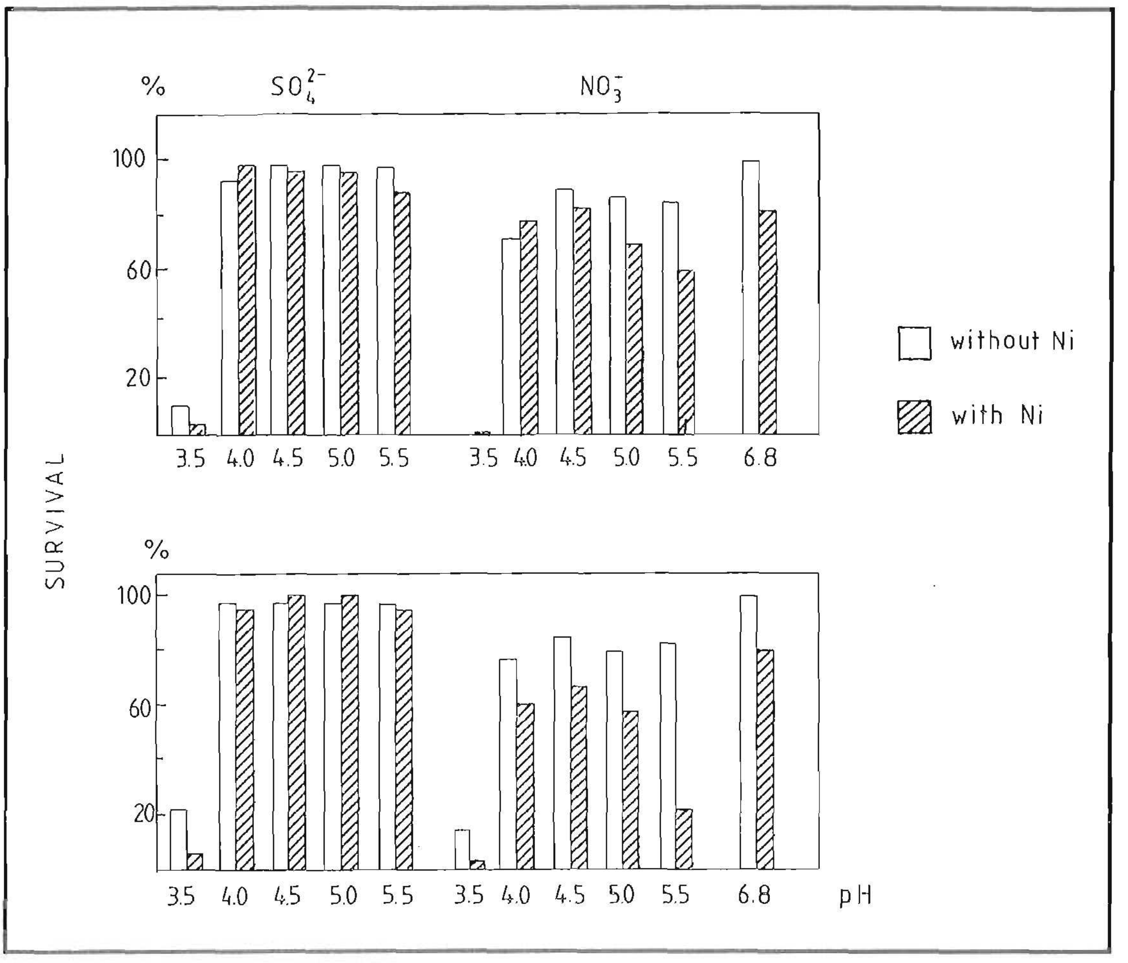

Fig. 7. Survival of Coregonus albula and C. lavaretus spawn at different pH levels.

4 CONCLUSIONS

It is obvious that the acidification process is a serious risk not only as an independent phenomenon, but also as the basis of more profound and dangerous processes involving the ecosystems of water bodies.

The essential intensification of copper toxicity upon the hydrobionts in an acidic environment was observed in this experiment. At lower pH levels the LC_{50} values decreased. However, the results of the nickel tests showed that LC_{50} values for nickel in acidic and neutral environments were not significantly different. The use of different acids (H_2SO_4, HNO_3, HCl) as acid agents as well as the use of water from different water bodies showed that nickel toxicity was dependent on the presence of hydrogen ions and the combination of complexes formed in water.

An estimation of the consequences of acidification needs to consider all possible transformations of substances which take place in water with respect to the trophic state and chemical composition of the water, as well as the toxico-resistance of the organisms.

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THE EFFECTS OF FOREST CLEAR-CUTTING AND SOIL PREPARATION ON THE WATER QUALITY OF SMALL FOREST BROOKS

Marketta Ahtiainen,
North Karelia Water and Environment District
P.O.Box 69,
FIN-80101 Joensuu, Finland

1 INTRODUCTION

Several wood-production programmes aim to increase the productivity of peatland soils. Rehabilitation of the degenerated forests and intensification of normal timber production have been implemented in Finland in recent years. However, the environmental aspects are widely neglected. Areas prepared for natural or artificial regeneration are usually treated by forest harrowing, screefing or ploughing in mineral soil. Drainage or hummocking and the earlier deep tillage was used in waterlogged areas. Soil preparation is now conducted after clear-felling in almost all cases (80 %) for better water balance and seedling production. Soil preparation is normally conducted 1 - 3 years after cutting. The consequent rupture of the soil surface can cause leaching of organic matter, nutrients and metals accumulated in the soil.

The Nurmes-study involved the monitoring of water quality and hydrology of brooks in six basins since 1978. All brooks were investigated in their untouched state for five years, after which clear cutting was carried out on two of the basins in 1983, leaving the Liuhapuro basin as reference (Ahtiainen 1988, Ahtiainen et al.1988, , Holopainen et al. 1989, Huttunen et al. 1988, 1990). At the second stage (summer 1986) soil preparation (forest ploughing, hummocking and drainage) was conducted in the clear-cut area of Murtopuro area and forest ploughing in the Kivipuro area. The effects of soil preparation on water quality have been reported e.g. by Kubin (1987), Rosen and Lundmark-Thelin (1986, 1987).

The main objectives of this study were to investigate changes in water quality and to quantify the annual load of nutrients, organic matter and iron in two cases: (1) after clear-cutting and soil preparation and (2) after clear-cutting and forest ploughing when a protective zone along the brook was left.

2 STUDY AREA AND TREATMENTS

The study brooks are situated in two separate areas in eastern Finland (Fig. 1). Murtopuro and Liuhapuro basins are situated in the district of Valtimo (63°45' N 28°30' E). The Kivipuro basin is located in Sotkamo (63°52' N 28°35' E) approximately 30 km apart. Their catchment areas are small (0.5 - 1.7 km^2) and their altitude (170 - 246 m a.s.l.) and slope similar (in detail see Ahtiainen et al. 1988, Holopainen et al. 1988). The drainage basins, forestry measures and the proportions of the drainage basins affected (%) are shown in Table 1.

The hydrology in these brooks has been published by Seuna (1988). Holopainen et al. (1989) and Huttunen et al. (1988, 1990) have investigated the effects of forestry operations on production biology of the forest brooks in the Nurmes research project.

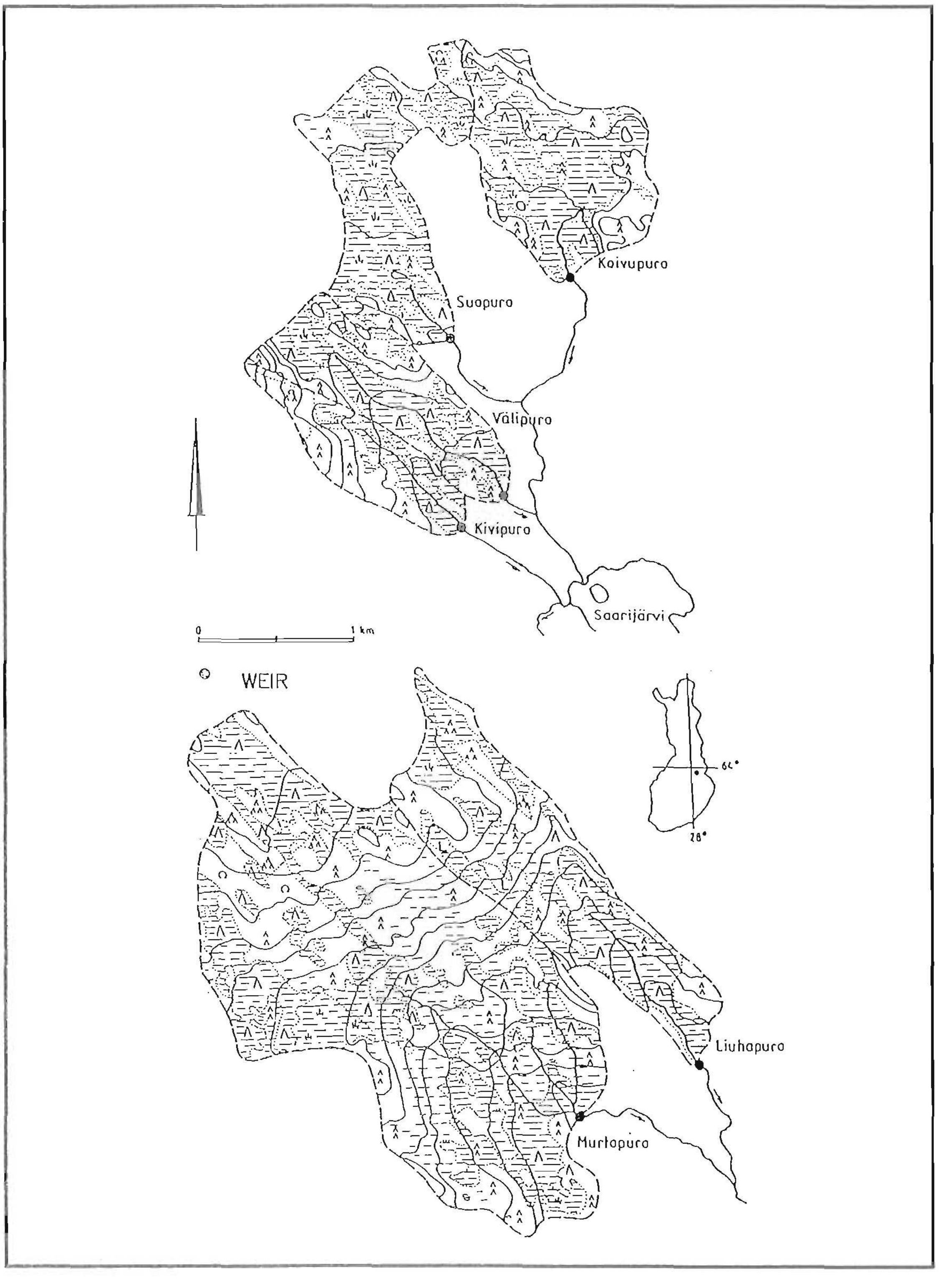

Fig. 1. Map of the study areas.

Table 1. Drainage areas and forestry operations per cent of the drainage basins affected.

Basin	Area km^2	% of the drainage basin	1982 - 1983	1986	1987
Murtopuro	4.94	58	Forest roads and ditches, 12 km clear-cutting 286 ha 31.8.82 - 21.6.83	Forest ploughing 80 ha, drainage 198 ha and hummocking 49 ha (2.6. - 11.12.86)	Planting
Kivipuro	0.54	56	Clear-cutting 30 ha, with protective zone (17.1. - 13.4.83)	Forest ploughing 32 ha (2. - 10.7.86)	Planting
Liuhapuro	1.65		No forestry operations, control site.		Planting

3 MATERIALS AND METHODS

The monitoring of water quality was started in 1978. The continuous discharge observations started simultaneously. Samples were taken biweekly from early May to the end of September, otherwise once a month. The sampling and water quality analyses were conducted according to the standard methods of National Board of Waters (1981, 1984). All analyses were made on non-filtred samples and suspended solids were concentrated by filtration through glass fibre filters (Whatman GF/C). The annual loads were calculated as described by Ahtiainen (1988).

4 RESULTS

During the growing season the mean water temperatures, as well as the maximum temperatures (> 10 °C), rose directly after clear-cutting and further after scarification in Murtopuro. In the Kivipuro basin with the protective zone along the brook no changes in water temperature were noted after the forestry measures.

The 3-year averages of total and phosphate phosphorus concentrations were 5-fold those during the calibration period following clear-cutting and still almost 4-fold in 1985 before the second stage treatment in Murtopuro (Table 2). The total and phosphate phosphorus concentrations remained high during the years after clear-cutting while the highest total and phosphate phosphorus concentrations were found in connection with the spring maximum runoffs after scarification, being 3-4- fold those during the reference period (Fig. 2).

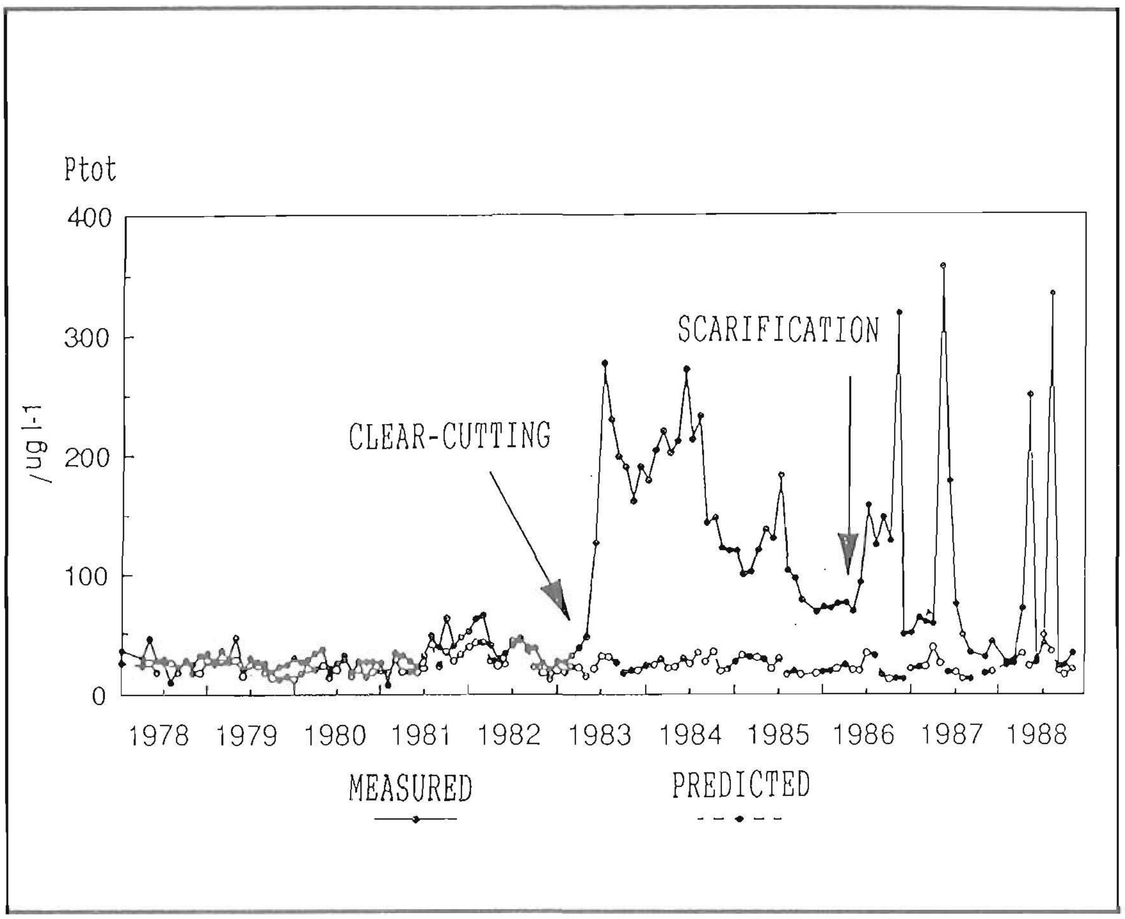

Fig. 2. Monthly mean concentrations of total phosphorus before (1978–82) and after clear-cutting (1983–86) and subsequent scarification (1986–88) in Murtopuro. The predicted values are calculated by the values of the reference brook.

The annual total phosphorus load in 1985 remained over 3–fold that durind the reference period. The 3–year annual mean of total phosphorus after clear–cutting (66 kg km^{-2} a^{-1}) was over 4– fold that during the reference period (15 km^{-2} a $^{-1}$). The annual load of total phosphorus remained nearly at the same level for at least three years after scarification in Murtopuro. The 3–year mean of phosphate phosphorus was nearly 6–fold after clear–cutting compared with the reference load, and still 4–fold after soil preparation in 1986–88 (Table 2, Fig. 3).

The total nitrogen load doubled after cutting and tripled after soil preparation as compared to the reference in Murtopuro. The increase in the 3–year mean of NO_3–N after scarification was as high as 10–fold that of the control period and 3–fold that of post–cutting period, and the increase in the 3–year mean of NH_4–N after scarification was over 6–fold that of the control period and twice that of the post–cutting period in Murtopuro.

The most harmful environmental effect after scarification was a noticeable increase in the loads of suspended solids, the 3–year mean being 83 tn km^{-2} a^{-1}, over 200–fold that of the reference time. The amount of fixed iron in suspended solids increased 3–fold at the same time (Table 2). The COD increase in the year of scarification did not exceed the COD of the clear–cutting year. During the two years after scarification the organic matter load diminished and almost reached the level of reference basins in the third year.

The protective zone along Kivipuro clearly reduced the impacts of clear-cutting and soil preparation (Table 2).

Table 2. Annual loads (kg km^{-2} a^{-1}) from the Murtopuro and Kivipuro basins before (1979-1982) and after clear-cutting (1983-1985) and subsequent soil preparation (1986-1988). The Liuhapuro results are quoted for reference. Note S-S as suspended solids (tn km^{-2} a^{-1}).

	N_{tot}	NO_3-N	NH_4-N (kg km^{-2} a^{-1})	P_{tot}	PO_4-P	Fe	COD	S-S (t km^{-2} a^{-1})
Murtopuro								
1979-82	**204**	**3.5**	**4.6**	**14.6**	**7.3**	**535**	**18.4**	**0.4**
1983	460	7.5	9.7	56.0	33.6	1146	35.7	0.5
1984	473	10.0	32.4	91.8	69.5	836	27.9	0.7
1985	356	14.4	15.6	48.7	27.5	657	22.9	0.6
1983-85	**430**	**10.6**	**19.2**	**65.5**	**43.5**	**880**	**28.9**	**0.6**
1986	824	26.6	22.4	74.7	18.5	2042	29.4	80.0
1987	456	19.6	20.3	62.6	35.9	927	15.6	69.1
1988	519	44.3	41.9	67.1	29.1	1412	17.1	101.1
1986-88	**600**	**30.2**	**28.2**	**68.1**	**27.8**	**1460**	**20.7**	**83.1**
Kivipuro								
1979-82	**157**	**1.3**	**2.7**	**6.9**	**1.6**	**257**	**13.1**	**0.4**
1983	295	1.2	3.1	10.5	1.3	393	24.9	0.5
1984	232	2.1	9.3	10.1	2.2	320	16.1	0.4
1985	150	0.8	2.0	7.3	1.3	198	10.7	0.4
1983-85	**226**	**1.4**	**4.8**	**9.3**	**1.6**	**304**	**17.2**	**0.4**
1986	222	2.2	3.0	6.9	1.0	296	16.3	0.2
1987	141	0.3	2.5	6.5	1.5	197	11.1	0.1
1988	183	1.9	2.6	8.5	2.0	240	13.7	0.2
1986-88	**182**	**1.5**	**2.7**	**7.3**	**1.5**	**244**	**13.7**	**0.2**
Liuhapuro								
1979-82	**201**	**2.8**	**3.4**	**10.0**	**3.1**	**440**	**17.4**	**0.4**
1983-85	**225**	**3.4**	**2.8**	**9.0**	**2.1**	**404**	**16.3**	**0.3**
1986-88	**200**	**-**	**2.6**	**7.8**	**1.9**	**384**	**15.4**	**0.2**

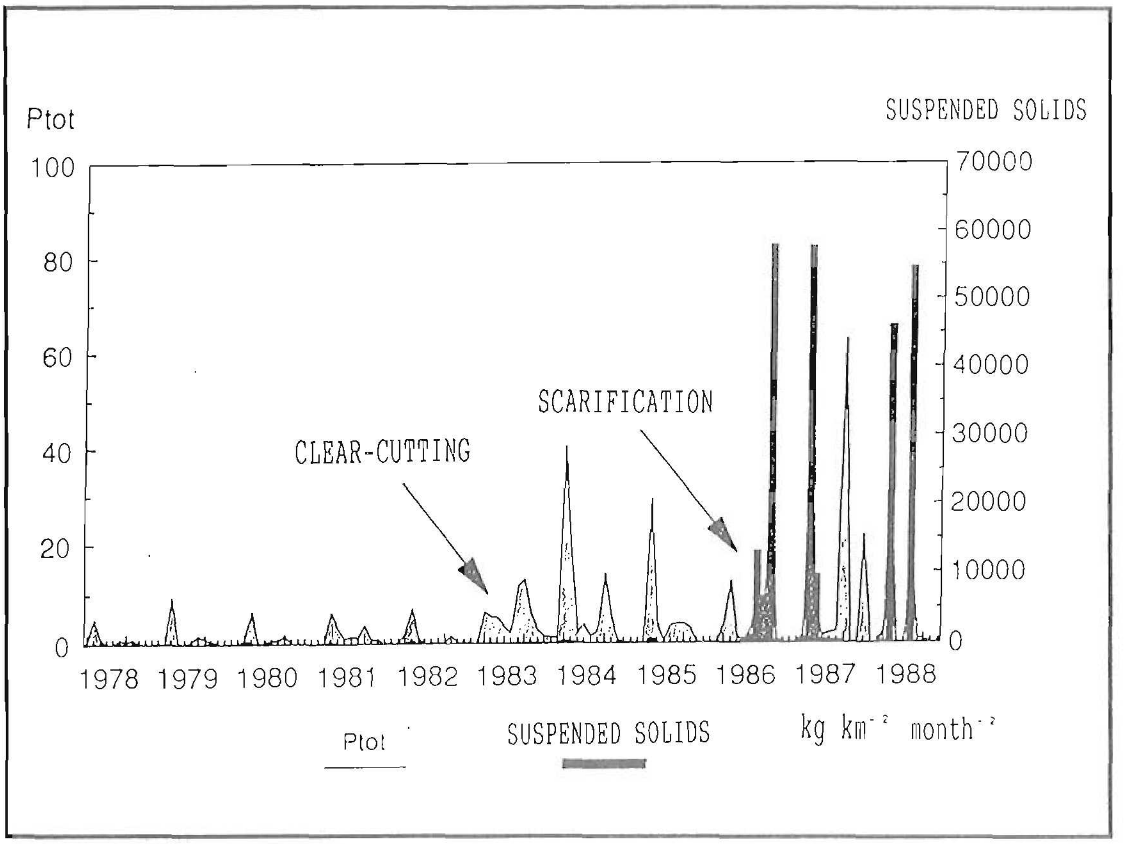

Fig. 3. Monthly mean loads of total phosphorus and suspended solids before (1978–1982) and after clear-cutting (1983–1986) and subsequent soil preparation (1986–1988).

5 DISCUSSION

The nutrient cycles in an disturbed forest ecosystem are to large extent closed, i.e. nutrient losses are minimal (Ahtiainen 1988, 1992). The nutrient loads from the reference basin Liuhapuro varied from 200 – 225 kg km^{-2} a^{-1} for total nitrogen and 8–10 kg km^{-2} a^{-1} for total phosphorus. These values agree well with the results reported from small forest drainage basins by Kauppi (1978) and Rekolainen (1989) as well as Swedish leaching losses from undisturbed forest soils, 3 – 8 kg km^{-2} a^{-1} (Bergquist et al. 1984, Grip 1982).

A three year interval was too short to regain the pretreatment concentrations for nearly all the water quality variables after clear–cutting. The COD was the only variable which nearly reached the original level in Murtopuro three years after clear–cutting. The load of suspended solids (0.6 tn km^{-2} a^{-1}) was only 1.5– fold the background situation after clear–felling in Murtopuro (Table 2) in contrast to the heavy erosion loads reported by Likens & Bormann 1974, Lynch et. al 1980. The total nitrogen load doubled, the NO_3–N load increased 3–fold and the NH_4–N load increased 4–fold during the 3–year period after cutting. Clear–cutting can cause a marked increase in nitrogen loads, especially in mineral soils (Bormann et al. 1968, Tamm et al. 1974, Wiklander 1981 and Rosen & Lundmark–Thelin 1987). Martin et al. (1984) also found that inorganic nitrogen compounds rose up to 4–fold after clear–cutting but found no increase when a protection zone was used, as we also saw in Kivipuro.

The large-scale cutting on peat soil in Murtopuro created a significant increase in the loads of total and phosphate phosphorus, which was reflected in the primary production of the brook (Huttunen et al. 1990). The rises of COD, Fe and different nitrogen variables were also marked. The loads increased due to the breaking of the tight materials cycles. In particular, autolysis in the root zone strongly affects leaching of phosphate phosphorus (Grip 1982). The ground water table rose nearly to the surface soil, which caused anaerobic conditions in the soil layer (Rodhe 1985). Both the changes in hydrology and the soil disturbance were important (Rosen 1982).

Kubin (1987) and Rosen & Lundmark-Thelin (1986) have reported rising nitrogen concentrations and loads after forest ploughing and scarification operations as was also found in Murtopuro after soil preparation.

The pattern of nutrient release from peat soils will depend on the net balance between solute inputs and outputs and any changes in storage within the peat. The provision of an outlet for mobilized nutrients, as in the case of peat drainage, will change the storage characteristics of peat. In the drained peat areas, the rapid fluctuation of the peat water table and the availability of an outlet for the mobilized nutrients produce a different pattern of nutrient release (Heathwaite 1990). The water table often fluctuates more widely in drained peat and this may accelerate nutrient release. The greatest impact of scarification was, however, the huge increase of suspended solids by over 200 times. Moreover, 1000 m^3 of eroded material has been dug from behind the weir during the 3 years after scarification in Murtopuro. Hynninen and Sepponen (1983), Kenttämies (1987), Sallantaus (1986) and Seuna (1982) have reported very high loads of particulate inorganic eroded material during the spring flood period and during heavy rain which could also be measured in Murtopuro.

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Air-borne pollution is the most serious environmental problem in many countries. The longdistance transport of pollutants has also made air-borne pollution an international problem and resulted in extensive research cooperation.

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